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THE LAWS GOVERNING THE RATE AT WHICH METALS DISSOLVE IN CONCENTRATED ACIDS

II. THE SOLUTION RATES AND DISSOLUTION POTENTIALS OF CHROMIUM AND IRON.

Ya. V. Durdin

As we have stated in our previous report [1], two types of curves $\underline{v}(\underline{c})$ are found when metals are dissolved in concentrated acids, representing the rate of dissolution of the metal as a function of the acid concentration: $\underline{v}(\underline{c})$ curves exhibiting a maximum and those without one.

It has been shown in our previous report [1] that curves possessing a maximum reflect the superposition of a secondary phenomenon - the precipitation of a deposit of a salt of the metal upon the latter's surface. The fundamental behavior patterns involved in the rates at which metals dissolve as a function of the acid concentration are therefore reflected by the curves having no maximum.

An essential factor is the fact that (as has been noted in the same report) the general shape of these curves is the same for various metals: Cd, Al, Fe, and Cr, the appearance of the $\underline{v}(\underline{c})$ curves reflecting the step-by-step variation of the dissolution rate with the acid concentration, while the curves approach a straight line in sulfuric acid.

Tsentnershver thought that the functions of $\underline{v}(\underline{c})$ obtained by him for the dissolution of cadmium [2], aluminum [3], and tin [4] could be represented by the equation:

$$\underline{v} = kc^{n}, \qquad (1)$$

where $\underline{n} = 4$ for Cd and 3 for Al. Since a function of this sort was wholly out of line with the variation of the specific conductance of hydrochloric acid with its concentration, Tsentnershver concluded that only alloys dissolved in accordance with an electrochemical mechanism, while the pure metals (which he assumed the Kahlbaum Cd and Al he had tested were) dissolve via a peculiar mechanism, which he called 'chemical', in which the metal is dissolved as a result of its interaction with the acid anion [5]. This led to a sharp duality in dealing with the rates of dissolution of metals, not only in concentrated acids, but in the general case as well, since it did not follow from Tsentnershver's hypothesis that his chemical mechanism could change to an electrochemical one in dilute acids or salt solutions.

These difficulties were aggravated by the lack of a definition of the line of demarcation between a pure metal and an alloy, inasmuch as Tsentnershver used the term 'pure metal' for the metals supplied by the Kahlbaum firm that he employed in his tests, though their purity is highly relative. It may be added that if we use the Tsentnershver mechanism, we have to assume that the dissolution of cadmium or tin in hydrochloric acid entails the simultaneous collision of four chlorine atoms with an atom of the metal in the space lattice, which is highly improbable. Moreover, Tsentnershver based his mechanism upon the fact

that the dissolution rates of the metals he investigated obeyed Equation [1]. According to that equation, log v must be a linear function of log c. But actually if we use Tsentnershver's own data on the dissolution rates of cadmium [2] and aluminum [3,6] in plotting a lg v - lg c curve, we get broken lines, the slopes of the various sections of these lines ranging from $n = 5.8$ to $n = 2.7$ in the interval from 6N to 12N HCl. The value of $n = 4$ used by Tsentnershver thus is some sort of mean of these values, possessing no definite physical significance. The same sort of picture is found in the case of aluminum.

In the present pape we endeavor to show that the patterns of behavior observed when chromium and iron are dissolved in hydrochloric and sulfuric acids conform to generalized electrochemical theory.

The Treatment of the Laws Governing the Dissolution Rates of Chromium and Iron in Hydrochloric and Sulfuric Acids as Based Upon Generalized Electrochemical Theory.

According to the data on the rates of dissolution of chromium and iron obtained in our laboratory [7,8], the rates at which these metals dissolve in hydrochloric and sulfuric acids may be regarded as unaffected by the diffusion process, provided the solution is stirred intensively enough. If we assume that the kinetic energy of the process of ion transfer between the cathodic and anodic areas via conductance is practically equal to zero, then the generalized electrochemical theory asserts that the dissolution rates of chromium and iron must be governed by the rates at which the electrode processes - the cathodic process in which hydrogen is evolved and the anodic process in which the metal ions leave the solution - take place.

The feasibility of explaining the behavior patterns governing the rates at which metals are dissolved in concentrated acids on this basis was first demonstrated in the author's paper 'The electrochemical mechanism of the dissolution of metals in acids' [9]. This paper, which dealt in general with the feasibility of handling the laws governing the dissolution rates of metals by means of the laws governing the rate at which electrode processes take place, quoted excerpts from the above-mentioned paper by A. Markiyevich and the present author on the rates at which chromium and iron dissolve in hydrochloric and sulfuric acids by way of illustrating this possibility, it being shown that the behavior patterns observed in the dissolution of chromium can be treated like the laws governing the rate at which the cathodic process of hydrogen evolution takes place. It was shown, in particular, that the exponential shape of the $v(c)$ curve for the dissolution of chromium in hydrochloric acid may be explained as a result of the decrease in the energy of hydration of the hydrogen ions in concentrated solutions of hydrochloric acid and a corresponding decrease in the energy of activation of their discharge.

In that same paper an experimental method of comparing the $v(c)$ curves for the rates of metal dissolution and the rates of the cathodic process of hydrogen evolution was employed to substantiate these assumptions. In this instance we made use of the circumstance that, according to our results [7], the dissolution potential of chromium referred to a saturated calomel electrode was practically constant throughout the range of 1N to 10N acid, this held for both the hydrochloric and the sulfuric acids. With this as a basis we ran tests in which we measured the rate of the cathodic evolution of hydrogen as a function of the concentration of the hydrochloric and sulfuric acids, the potential of the cathode referred to the saturated calomel electrode being kept constant. A comparison of the resultant $v(c)$ curves for the

for rate of dissolution of chromium indicated that the shapes of the two curves were fully alike qualitatively. These experiments, made to plot the $\underline{v}(\underline{c})$ curves for the cathodic evolution of hydrogen, were preliminary tests. To corroborate our findings we made more precise determinations of the same function with a dropping mercury electrode; the qualitative nature of these curves was found to be the same as in the preliminary tests. The $\underline{v}(\underline{c})$ curves secured in these tests are plotted in Fig. 1. For convenience in comparison, the $\underline{v}(\underline{c})$ curves for the dissolution of chromium and iron taken from our papers written in collaboration with A. Markievych [7] and M. Oranskaya [8] are reproduced in Fig. 2 (the experimental points being omitted for the sake of simplicity). Comparison of these graphs clearly indicates the complete qualitative similarity between the shape of the $\underline{v}(\underline{c})$ curves for the dissolution of the metals and that of the corresponding curves for the velocity of the cathodic evolution of hydrogen.

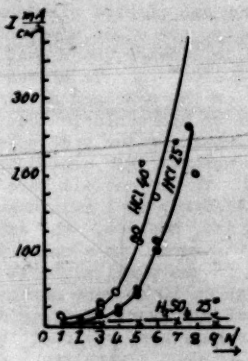

Fig. 1

We thus could regard it as an established fact that the qualitative nature of the $\underline{v}(\underline{c})$ curves, without any maximum, plotted for the dissolution of metals in hydrochloric and sulfuric acids, not only does not contradict the generalized electrochemical theory, but, on the contrary, is in full accordance with it.

For further study of this problem it was desirable to shift from a qualitative to a quantitative comparison of these same behavior patterns. With this as our objective, we began to make preparations for further, more precise experiments to determine the variation of the velocity of the cathodic evolution of hydrogen with the concentration of hydrochloric and sulfuric acids; this project was interrupted by the war, however.

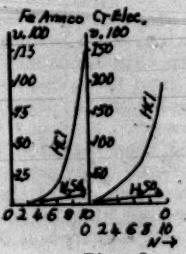

Fig. 2

At the present time we are making use of the data on hydrogen overvoltage provided in the papers by Z. Iofa and A.N. Frumkin [10, 11, 12] for this purpose.

Attempted Quantitative Comparison of the Rate of Dissolution of Chromium and Iron as a Function of the Acid Concentration with the Corresponding Cathodic Process Rates

The cited papers by Z. Iofa and A. Frumkin give figures for the hydrogen overvoltage at mercury and lead cathodes in hydrochloric, sulfuric, hydrobromic, and perchloric acids of various concentrations. In order to derive the velocity

of the cathodic evolution of hydrogen as a function of the concentration of the respective acid for a fixed cathode potential referred to the saturated calomel electrode, which we were interested in, we had to have the equilibrium potentials of a hydrogen electrode referred to a saturated calomel electrode in these same solutions.

The determinations of these potentials for solutions of hydrochloric and sulfuric acids at concentrations ranging from 1N to 0.1N and at temperatures of 20, 40, and 60°C were made by V.G. Levina under the supervision of the author.

These measurements were made in parallel tests run with systematically platinized and checked platinum electrodes. As in our metal dissolution experiments, the other electrode was a saturated calomel electrode. The tests were run in a water thermostat, the temperature of which was kept constant within ±0.1°C. To prevent the hydrogen chloride that collected under the dome of the hydrogen electrode from being blown out of the concentrated solutions of hydrochloric acid, the hydrogen was first passed through a vessel containing the same solution of hydrochloric acid and immersed in the same thermostat. The acid concentrations were determined before and after each run. The potentials were measured by the usual compensation method with an accuracy of 1 mv, inasmuch as high precision was unnecessary for our purposes and, besides, the experimental margin of error proved to be greater than that figure. As a rule, the discrepancy between the potentials as measured in two parallel tests did not exceed 1-3 mv, though discrepancies of as much as 10 mv were observed in some tests in which concentrated solutions were employed. Neither damage to nor poisoning of the hydrogen electrode can have been responsible for these discrepancies, inasmuch as identical results were always secured when the hydrogen electrode was replaced by another. We suppose the reason behind these potential fluctuations is fluctuation in the value of the diffusion potential within the electrolytic switch. The electrolytic switch used was a Π-shaped glass tube, sectioned off at its midpoint by a three-way glass stopcock. Before a run was started, the acid solution to be used in the test was pumped into one of the tubes connected to this stopcock, while a saturated solution of potassium chloride was pumped into the other. The stopcock itself was always moistened with the saturated solution of potassium chloride. The stopcock was kept closed during the measurement. We found that if the electrolytic switch was withdrawn, emptied, and then refilled (or simply replaced by a similar switch) after the potential of the hydrogen electrode had been measured, the potential of the hydrogen electrode would hardly vary at all, 1-3 mv at most, though greater fluctuations, as high as the indicated 10 mv, were found in some instances. The potentials measured at 20°C in these tests are listed in Table 1.

Using the figures in Table 1 for the equilibrium potential of the hydrogen electrode and the figures for the hydrogen overvoltage given in Z.A. Iofa's paper for various concentrations of hydrochloric and sulfuric acids, we can readily calculate the variation of the velocity of the cathodic evolution of hydrogen with the concentrations of these acids, provided the cathode potential referred to the saturated calomel electrode is kept constant. We shall begin by considering the case of hydrochloric acid. The figures covering the evolution of hydrogen at a lead cathode are given in Table 2, and at a mercury cathode in Table 3.

In these tables:

1) N = normality of the acid.

2) $\underline{E}^{o}$ = equilibrium potential of the hydrogen electrode (referred to a saturated calomel electrode) in the acid of given concentration at 20°. The values of $\underline{E}^{o}$ are taken from Table 1. We stipulate that in the present paper it will be more convenient for us to introduce different notation for potentials referred to the calomel electrode, which we shall denote by $\underline{E}$, and for the potential jump at the metal-solution boundary, for which we retain the notation φ.

Table 1.

Equilibrium Potentials of a Hydrogen Electrode (Referred to a Saturated Calomel Electrode) in Hydrochloric and Sulfuric Acids at 20 °C (With Reversed + Sign)

	N	1	2	3	4	5	6	7	8	9	10
E^{o} Volts	HCl	0.249	0.231	0.217	0.204	0.194	0.184	0.175	0.166	0.158	0.149
	H_2SO_4	0.263	0.249	0.236	0.228	0.222	0.215	0.208	0.202	0.197	0.192

Table 2

1	2	3	4	5	6	7
N HCl	E^{o}	$\Delta\varphi'$	b	E	$\Delta\varphi''$	W
1	0.249	1.055	0.119	1.304	1.055	1
3	0.217	1.005	0.142	1.304	1.087	3.8
5	0.194	0.935	0.140	1.304	1.110	18
7	0.175	0.865	0.138	1.304	1.129	82
10	0.149	0.755	0.135	1.304	1.156	930

Table 3

1	2	3	4	5	6	7
N HCl	E^{o}	$\Delta\varphi'$	b	E	$\Delta\varphi''$	W
1	0.249	0.940	0.119	1.189	0.940	1
3	0.217	0.863	0.140	1.189	0.972	6
5	0.194	0.770	0.124	1.189	0.995	65
7	0.175	0.714	0.114	1.189	1.014	430
10	0.149	0.660	0.106	1.189	1.041	4000

3) $\Delta\varphi'$ = hydrogen overvoltage at the mercury or lead cathode in hydrochloric acid at the stated concentration, the current density being $I = 10^{-4}$ amp/sq cm. We have taken the values of $\Delta\varphi'$ from papers by Z. Iofa [12], Z. Iofa [10], and Z. Iofa and A. Frumkin [11].

4) b = a constant from Tafel's equation. The values of b were taken from the same papers by Z. Iofa.

5) E = the constant cathode potential for which the C.D. is computed for various concentrations of hydrochloric acid. The value of E was taken as the cathode potential in 1N hydrochloric acid at a C.D. of $I = 10^{-4}$ A/cm^2. For the lead electrode, we see from Table 2 that E is 0.249 + 1.055 = 1.304 V, while Table 3 shows that for the mercury electrode E = 0.249 + 0.940 = 1.189 V.

6) $\Delta\varphi''$ = the hydrogen overvoltage in hydrochloric acid of various concentrations for the potential E.

7) W = the comparative increase in the rate of the cathodic process in shifting from 1N hydrochloric acid to hydrochloric acid of the stated concentration. The values of W can be readily found from the values of $\Delta\varphi'$ and $\Delta\varphi''$ in the table columns and from Tafel's equation:

$$\Delta\varphi = a + b \log I,$$

whence

$$\frac{\Delta\varphi'' - \Delta\varphi'}{b} = \log \frac{I''}{I'} = \log W,$$

where I' is the C.D. corresponding to a constant value of the cathode potential E in hydrochloric acid, and I'' is the C.D. for the same value of E in hydrochloric acid of the stated concentration. The analogous figures for the cathodic evolution of hydrogen at a lead electrode in sulfuric acid are given in Table 4.

Table 4

1	2	3	4	5	6	7
N H_2SO_4	E^0	$\Delta\varphi'$	b	E	$\Delta\varphi''$	W
1	0.263	1.060	0.119	1.325	1.061	1
3	0.236	1.056	0.119	1.325	1.089	1.9
5	0.222	1.054	0.120	1.325	1.103	2.6
8	0.202	1.050	0.120	1.325	1.123	4.0

The values of E^0 in this value are taken from Table 1. The values of $\Delta\varphi$ and b are taken from the paper by Z. Iofa [12], p.120, Table 4.*

Figure 3 reproduces the curves that express the variation of W with the concentration of hydrochloric and sulfuric acids for a lead cathode. These curves have been plotted from the figures in Tables 2 and 4. At first sight these curves are quite similar to those reproduced in Fig. 2, though it is not hard to see that this is not quite the case quantitatively speaking. This is strikingly illustrated by the figures in Table 6. This table has been compiled from the data in Tables 2,3, and 5. Table 5 gives the figures for the rates of dissolution of chromium and iron (Armco and light sheet) in hydrochloric and sulfuric acids of various concentrations, according to the findings reported in our papers with A. Markiyevich [7] and M. Oranskaya [8]. As always, the velocity v in this

*It should be stated that in Iofa's paper the hydrogen overvoltages at a lead electrode in H_2SO_4 are given only for 0.1N, 1N, 8N, 15N, and 20N H_2SO_4. We see from Table 5 that the total change in overvoltage is 0.01 volt from 1N to 8N sulfuric acid. Using this figure, we calculated $\Delta\varphi$ for 3N and 5N H_2SO_4, setting $\Delta\varphi/\Delta$ = const = 0.0012 though we could have set $\Delta\varphi'$ = const for this case without any special loss in our calculations. In the range from 8N to 15N H_2SO_4, the change in the hydrogen overvoltage is somewhat higher, totaling 0.055 volt, according to the data in the above paper, the proportion of the change in overvoltage attributable to the 8-10N H_2SO_4 range being unknown, so that in our calculations we confined ourselves to the 1N - 8N sulfuric acid range.

table is expressed as cubic centimeters of hydrogen evolved per minute per sq cm of metal surface. Table 6 gives the relative rates W for these metals and for the cathodic processes, the values of W in Section I of this table representing the ratio of the rate of dissolution of the given metal or the rate of the cathodic process in hydrochloric acid of the stated concentration to the rate in 1N acid, while in Section II W represents the ratio of the rate in acid of the stated concentration to 5N acid. The figures in Table 6 show that, notwithstanding the outward similarity of the v(c) curves, the extent of the change in velocity with acid concentration is different in every case, the rate of metal dissolution rising much more slowly than the rates of the cathodic processes. This difference is diminished at high concentrations of hydrochloric acid, as we see in Section II of the table, the discrepancy being least for the Armco iron.* An altogether different state of affairs prevails in the sulfuric acid, as we see from Table 7, which lists the values of W, representing the ratio of the velocity of the cathodic process or the metal dissolution rate in sulfuric acid of the stated concentration to the corresponding rates in 2N sulfuric acid (the rate at which iron dissolves in 1N sulfuric acid was not measured).

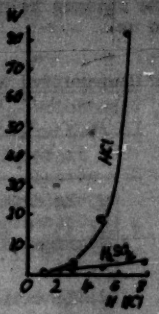

Fig. 3

Table 5

Dissolution Rate of Chromium and Iron in Hydrochloric and Sulfuric Acids

(Chromium at 40°, iron at 60°**)

Hydrochloric Acid

Acid normality	1	2	3	4	5	6	7	8	9	10 N
v·10³ Chromium	7.3	11(s)	17	24	33	45	66	95	125	190
Armco Iron	-	-	-	2.3	5.5	15	30	50	77	126
Light sheet iron	8.0	13(s)	17	24	36	56	85	130	230	430

Sulfuric Acid

Acid normality	1	2	3	4	5	6	7	8	9	10 N
v·10³ Chromium	4.3	5.7	6.6	7.5	8.4	9.4	11.0	12.5	14.5	16.5
Armco Iron	-	(1.8)	(2.5)	(3.0)	(4.0)	(4.5)	(5.5)	(6.4)	(7.0)	(8.0)*
Light sheet iron	-	12.5	16.0	20	25	30	35	40	46	52

We see in Table 7 that in sulfuric acid the velocities of all the processes we have been considering change comparatively slowly with acid concentration,

*As will be shown in a forthcoming paper, this fact may be due to a drop in the rate at which Armco iron dissolves at comparatively low acid concentrations, due to secondary phenomena.

**The figures for Armco iron in sulfuric acid are preliminary, as was stipulated in the paper in question [8].

the changes being approximately identical*, which is of especial interest to us.

Table 6

Comparative Rates of Dissolution of Metals and of Cathodic Evolution of Hydrogen in Hydrochloric Acid

	Acid normality	1	3	5	7	10N
I	$\underline{W}$, Hg cathodic process	1	6.1	65	480	4000
	$\underline{W}$, Pb cathodic process	1	3.8	18	82	930
	$\underline{W}$, light sheet Fe	1	2.1	4.5	10.6	54
	$\underline{W}$, Cr	1	2.3	4.5	9.0	26
II	$\underline{W}$, Hg cathodic process	-	-	1	7.4	62
	$\underline{W}$, Pb cathodic process	-	-	1	4.5	52
	$\underline{W}$, light sheet Fe	-	-	1	2.4	12
	$\underline{W}$, Armco Fe	-	-	1	5.5	23
	$\underline{W}$, Cr	-	-	1	2.0	5.8

Table 7

Acid normality	2	3	5	8
$\underline{W}$, Pb cathodic process	1	1.3	1.8	2.8
$\underline{W}$, light sheet Fe	1	1.3	2.0	3.2
$\underline{W}$, Armco Fe	1	(1.3)	(2.1)	(3.5)
$\underline{W}$, Cr	1	1.2	1.5	2.2

Summing up, we may say that although there is a marked qualitative analogy between the $\underline{v}(\underline{c})$ curves for metal dissolution and those for the cathodic evolution of hydrogen, there is a considerable quantitative difference between the rates at which these process rates change with the concentration of hydrochloric acid, the cathodic process rates rising with the acid concentration more rapidly than do the metal dissolution rates in the instances we have investigated. In sulfuric acid, on the other hand, we have a fairly satisfactory quantitative, as well as qualitative correspondence between the $\underline{v}(\underline{c})$ functions for the dissolution of the various metals and those for the cathodic evolution of hydrogen.

The Causes Governing the Variation of the Rates at Which Chromium and Iron Dissolve With the Concentration of Hydrochloric and Sulfuric Acids

The foregoing makes it evident that the explanation of these causes must be based upon the laws governing the velocity of the cathodic evolution of hydrogen in concentrated solutions of hydrochloric and sulfuric acids.

We can use the experimental findings and the theory of hydrogen overvoltage in concentrated acids set forth in the cited papers by Z. Iofa and A. Frumkin.

*It should be stated that the potential of chromium was practically identical in both hydrochloric and sulfuric acids, as has been demonstrated in our researches on chromium and iron [7,8]; the same holds true of the potential of Armco iron in hydrochloric acid. In sulfuric acid, the potential of Armco iron dropped slightly, by some 20 mv, in the transition from 2N to 10N sulfuric acid; the potential of light sheet iron, measured at the start of the test, changed by the same amount. The feasibility of ignoring this slight change in potential is dealt with in our forthcoming papers.

In these papers [10,11] an equation is derived for the velocity of the cathodic evolution of hydrogen in concentrated acids:

$$\bar{v} = \text{const } [H] \underline{f}_{H^+}^{\alpha'} e^{\frac{[\alpha\varphi+\psi_1(1-\alpha)]F}{RT}} \qquad (2)^*$$

In Equation (2) $[H^+]$ is the hydrogen-ion concentration in the solution: $\underline{f}$ is the activity coefficient of these ions; φ is the 'metal-solution' potential; ψ_1 is the sharp potential gradient between the layer at a distance of one ionic radius from the metal's surface and the solution; if ψ' is the sharp potential gradient in the Helmholtz double layer, then $\varphi = \psi' + \psi_1$; α is a constant, usually assumed to equal 0.5; α' is also a constant, whose value is likewise close to 0.5, according to the experiments made by Iofa and Frumkin [11], p. 281.

According to Equation (2), in concentrated solutions a change in the hydration energy of the hydrogen ions and an adsorption of the ions in the boundary layer** may affect the kinetics of discharging these ions, as well as a change in cathode potential φ and in the hydrogen-ion concentration $[H^+]$. The factor $\underline{f}^{\alpha'}$ in Equation (2) makes allowance for the effect of a change in the hydration energy of the hydrogen ions upon the velocity of the cathode process. In this light, the value of $\alpha' = 0.5$ signifies that a change in the hydration energy of a hydrogen ion has the same effect upon the energy level of the transitional discharge state of the hydrogen ion as does a change in the energy level of the hydrogen ion due to a change in the cathode potential ($\alpha = 0.5$).

The effect of adsorption of the anions is represented by the potential ψ_1. As shown in the researches of Z. Iofa and A. Frumkin, the expression they secured for the hydrogen overvoltage by a suitable transposition of Equation (2) makes it very easy to describe and explain the qualitative picture existing in the complicated system of behavior patterns manifested by hydrogen overvoltage in concentrated acids. This equation cannot, however, be regarded as quite accurate, quantitatively speaking. It may be that this inaccuracy is due in part, as has been indicated in that same paper [11], to the fact that the adopted representation of the double layer is still too crude, but, in addition, the use of this equation for precise quantitative computations is also complicated by the fact that the activity of the individual ion (hydrogen), an unknown factor, enters into the equation.

In their papers, Z. Iofa and A. Frumkin have on occasion made an attempt to escape this difficulty by using the mean activity of hydrochloric acid instead of the activity of the hydrogen ion. It is admitted that from the quantitative standpoint such a substitution is likewise insufficiently rigorous. Lastly, this equation cannot be used for quantitative calculations in most cases when nonmercury cathodes are employed, owing to our ignorance of the value of ψ_1. At first glance, the use of Equation (2) in dealing with the laws governing the rates at which metals dissolve involves even greater difficulties, since, in addition to what has been outlined above, any change in the acid concentration will affect the diffusion potential at the boundary between the acid and the potassium chloride solution (in the calomel electrode circuit). As a result, the changes in the cathode potential, measured with reference to the calomel electrode, may differ by an appreciable and unknown amount from the changes of the potential φ entering into Equation (2). It might well be thought that the sum total of all

*In the cited papers by Z. Iofa and A. Frumkin, φ and ψ_1 have the opposite sign in this equation.

**More precisely, the anion concentration in the adsorption layer.

these difficulties would not merely make it wholly impossible to use Equation (2) for the qualitative treatment of the laws governing the rate at which a metal dissolves, but might even interpose considerable uncertainty in their qualitative elucidation.

Upon closer examination of the problem, however, we find that Equation (2) may be so transformed for dealing with the problems with which we are concerned as to eliminate the difficulties arising from the unknown activity of the hydrogen ions and the diffusion potential, thus making use of this equation considerably easier.

In this transformation, we set $\alpha = \alpha' = 1/2$ in Equation (2) and assume that $[H^+]^{1/2} \cdot f^{1/2} = [H^+]^{1/2} \cdot a^{1/2}$, where a is the activity of the hydrogen ion. We can then rewrite Equation (2) as follows:

$$v = \text{const}\ [H^+]^{1/2} \cdot a^{1/2} \cdot e^{\frac{F\varphi}{2RT}} \cdot e^{\frac{F\psi_1}{2RT}} \qquad (3)$$

We then agree to consider the relative velocity W, discussed above, rather than the absolute velocity. From Equation (3), we get the logarithm of W as:

$$\ln W = \frac{1}{2} \ln \frac{[H^+]'}{[H^+]} + \frac{1}{2} \ln \frac{a'}{a} + \frac{F\Delta\varphi}{2RT} + \frac{F\Delta\psi_1}{2RT} \qquad (4)$$

where

$$W = \frac{v'}{v}\ ;\ \Delta\varphi = \varphi' - \varphi;\ \Delta\psi_1 = \psi_1' - \psi_1.$$

In these equations the variables bearing a prime refer to the acid of stated concentration, those without a prime mark referring to the acid of standard concentration, for which we assume that W equals unity. We denote the diffusion potential at the boundary between the acid and the saturated solution of potassium chloride by φ_D, so that:

$$E' - E = \Delta E = \Delta\varphi + \Delta\varphi_D. \qquad (5)$$

where $E' - E$ is the difference between the cathode potential (referred to the saturated calomel electrode) in the acid solution of given concentration (E') and that in the standard solution (E); $\Delta\varphi$ is the corresponding difference in the sharp potential gradient at the metal-solution boundary; and $\Delta\varphi_D$ is the corresponding difference at the liquid-liquid boundary. Provided the cathode potential is constant, referred to the calomel electrode, i.e., provided $\Delta E = 0$, we get:

$$\Delta\varphi = -\Delta\varphi_D.$$

Inserting this value of $\Delta\varphi$ in Equation (4), we get an expression for $\ln W$ when the cathode potential referred to the saturated calomel electrode is constant:

$$\ln W = \frac{1}{2} \ln \frac{a'}{a} + \frac{\Delta\psi_1 F}{2RT} + \frac{1}{2} \ln \frac{[H^+]'}{[H^+]} - \frac{F\Delta\varphi_D}{2RT} \qquad (6a)$$

or when $\Delta\psi_1 = 0$

$$\ln W = \frac{1}{2} \ln \frac{a'}{a} + \frac{1}{2} \ln \frac{[H^+]'}{[H^+]} - \frac{F\Delta\varphi_D}{2RT} \qquad (6b)$$

We do not know the change in the diffusion potential, which is a factor in this equation. Ignorance of this variable makes it impossible to determine the value of $\ln a'/a$ from the data for the equilibrium potential of the hydrogen electrode in the corresponding acid solutions. But in this case these two difficulties cancel each other out. In fact, the difference between the two equilibrium hydrogen-electrode potentials, referred to the saturated calomel electrode, in these two acid solutions is:

$$\Delta E^\circ = \Delta\varphi^\circ + \Delta\varphi_D,$$

while

$$\Delta\varphi^\circ = -\frac{RT}{F} \ln \frac{a'}{a},$$

so that

$$\ln \frac{a'}{a} = -\frac{F}{RT}\Delta E^\circ + \frac{F}{RT}\Delta\varphi_D.$$

Substituting this expression for $\ln \frac{a'}{a}$ in Equation (6a) and combining the $\frac{F}{RT}\Delta\varphi_D$ terms, we get:

$$\ln W = \frac{F}{2RT}\Delta E^\circ + \frac{F}{2RT}\Delta\psi_1 + \frac{1}{2}\ln\frac{[H^+]'}{[H^+]} \qquad (7)$$

or

$$\log W = \frac{1}{2}\left(\log\frac{[H^+]'}{[H^+]} - \frac{\Delta E^\circ F'}{RT} + \frac{\Delta\psi_1 F'}{RT}\right) \qquad (8a)$$

At $\Delta\psi_1 = 0$,

$$\log W = \frac{1}{2}\left(\log\frac{[H^+]'}{[H^+]} - \frac{\Delta E^\circ F'}{RT}\right), \qquad (8b)$$

where $F' = F \cdot 0.434$.

Equation (8) is therefore largely free of the uncertainties involved in the use of Equation (2).

The paper by Z. Iofa and A. Frumkin [11] gives values of ψ_1 for a mercury electrode. Using these values, we can make a sample calculation of W_{Hg}. This calculation has no special significance for us. We could have confined ourselves to Equation (8) for the qualitative inferences with which we are concerned. We perform this calculation largely to obtain a clearer idea of the problem*.

The values needed for this calculation are listed in Table 8. The values of ψ_1 have been taken from the paper by Z. Iofa and A. Frumkin [11], though with a plus sign, as we have stipulated, rather than with a minus sign as given in that paper. The values of ΔE° have been calculated from the data in Table 1, while the values of $W_{exper.}$ have been taken from Table 3. We obtained the values of $W_{calc.}$ from Equation (8).

Table 8

	1	3	5	7	10
ψ'	0.078	0.149	0.206	0.277	0.348
$\Delta\psi_1/0.058$	0	1.22	2.21	3.44	4.66
$\Delta E^\circ/0.058$	0	0.552	0.948	1.28	1.72
$\lg\frac{H^+}{H}$	0	0.484	0.703	0.848	1.00
W calc.	1	13	85	600	5000
W exper.	1	6	65	430	4000

The figures in Table 8 indicate that the values of $W_{calc.}$ are in good agreement with those of $W_{exper.}$ We see from this table that the rapid rise in the velocity of the cathodic evolution of hydrogen at a mercury cathode with increasing concentration of sulfuric acid, represented by an exponential curve, is governed chiefly by a rise in the value of ψ_1, representing the effect of anion adsorption. The potential change ΔE°** which is probably governed by an increase in the activity of the

*It should be noted that the values of ψ_1 cited in the paper by Z. Iofa and Frumkin are for potentials at the maximum on the electrocapillary curve, rather than a constant potential referred to the calomel electrode. Not too much importance need be attributed to this fact in the present case, inasmuch as the very same paper states that the decrease of the hydrogen overvoltage in concentrated acid solutions is only slightly affected by the potential of the cathode.

**The foregoing indicates that the variable ΔE° likewise covers the change in the diffusion potential at the liquid-liquid boundary.

hydrogen ions, likewise exerts an appreciable effect. The least effect is produced by an increase in the concentration of these ions* . These conclusions are in general agreement, of course, with those inferred in the cited papers by Z. Iofa and A. Frumkin from these authors' findings on the hydrogen overvoltage at a mercury cathode in hydrochloric acid.

As we see in Table 2, the velocity rises somewhat less with a lead cathode than with a mercury one as we pass from 1N to 10N hydrochloric acid. Equation (8a) indicates that the reason for this must be a smaller change in the value of ψ_1 when a lead electrode is used. When sulfuric acid is used, the anion adsorption in the acid concentration range up to 8N apparently has no effect upon the hydrogen overvoltage at a lead cathode, according to the findings reported in the same paper by Z. Iofa [12], p. 120-121. What is more, in sulfuric acid the magnitude of ΔE^* is likewise somewhat smaller than in hydrochloric acid, as we see in Table 1. Lastly, it must be thought that the hydrogen-ion concentration also increases less rapidly in sulfuric acid as the acid concentration is raised than is the case in hydrochloric acid. This makes wholly understandable the highly characteristic difference between the v (c) curves for the velocity of the cathodic evolution of hydrogen in hydrochloric and sulfuric acids - an exponential function in the case of hydrochloric acid and a nearly linear one for sulfuric acid. Moreover, if we assume that anion adsorption has practically no effect upon the velocity of the cathodic process in sulfuric acid, we must shift from Equation (8a) to Equation (8b) for sulfuric acid, the latter equation containing variables that are solely functions of the state of the solution and are unaffected by the nature of the cathode. This makes the equality between the relative velocities of the cathodic evolution of hydrogen at a lead cathode and the relative dissolution rates of chromium and iron that we had observed in sulfuric acid fully understandable as well. We therefore see that the basic set of laws governing the variation of the rates at which chromium and iron dissolve with the concentration of hydrochloric and sulfuric acids may be satisfactorily explained by means of the laws governing the velocity of the cathodic evolution of hydrogen in these acids. There are other facts that demand further consideration, however. One of them is the marked difference between the values of W for the velocities of the cathodic process and lead and mercury electrodes and the rates at which chromium and iron dissolve (in hydrochloric acid), referred to above. We assume that this fact may be explained in two ways:

1) On the assumption that the factors controlling the kinetics of the dissolution of chromium and iron are the electrode processes, we must assume that the adsorption of an anion will have a lesser effect, for one reason or another, upon the velocity of the cathodic evolution of hydrogen during the dissolution of chromium and iron than when the cathodic evolution of hydrogen takes place at the surface of a mercury or lead cathode. In the simplest case, this difference may be simply ascribed to a difference in the nature of the metals themselves. We assume, however, that in addition to this cause, another factor may play a part in this case, namely, the fact that during the dissolution of a metal hydrogen is evolved at a continuously renewed surface, while in the case of a mercury or lead cathode, this evolution takes place at the surface of a metal that does not dissolve.

*Since HCl is a strong electrolyte (and chiefly because we have no other data), we assume that the change in the concentration of the H ions is proportional to the change in the overall acid concentration.

2) Another possible explanation of the same phenomenon is an increase in the kinetic energy of the ion-transfer process in concentrated solutions of hydrochloric acid due to conductance, i.e., an increase in the IR drop of the potential between the cathodic and anodic areas of the metal surface. Which of these two explanations is satisfactory will be considered at greater length in our forthcoming papers, which will likewise deal with the problem of the potentials of dissolving chromium and iron. Lastly, we should like to comment on still another fact. The findings reported in our papers written with Markiyevich [7] and Oranskaya [8] on the potentials of dissolving chromium and iron, the entrance of iron ions (and apparently of chromium ions as well) into solution is accompanied by appreciable anodic polarization - of the order of 0.2 to 0.26 volt. This makes it impossible to equate the kinetic energy of the anodic process to zero. This fact does not contradict the conclusions we have reached above. The behavior patterns governing the dissolution rate of a metal, provided the kinetic energies of the cathodic and anodic processes are comparable, may be handled either by means of the derived general equation by simultaneously solving the equations for the rates at which the cathode and anode processes take place, as was done in the papers by A.I. Shultin [13, 14], or by using one of these equations, say the equation for the cathodic process, and experimentally determining the potential of the dissolving metal, as has been done in the present paper. The two methods are essentially identical though there is a substantial difference between them in practice.

The first method is more complete, fundamentally speaking, since this actually allows for the behavior patterns controlling both processes, whereas in the second method the behavior patterns that govern the velocity of the anodic process are allowed for formally via the changes in the potential of the dissolving metal. Unfortunately, the first method suffers at present from the handicap that we have to know not only the behavior patterns and the equations governing the velocity of the cathodic evolution of hydrogen, but also those governing the anodic process in which the metal ions enter solution, about which much less is known at the present time. What is more, the derivation of the general equation by simultaneously solving the individual equations for the velocities of the cathodic and anodic processes is extremely complicated, as may be seen from the paper by A. Shultin; this, too, compelled us to employ the second method.

SUMMARY

1. The feasibility of dealing with the behavior patterns governing the dissolution rates of chromium and iron in concentrated solutions of hydrochloric and sulfuric acids (ranging from 1N to 10N) on the basis of the generalized electrochemical theory has been discussed.

2. It has been shown that the $v(c)$ curves representing the variation of the chromium and iron dissolution rates with the concentration of the hydrochloric and sulfuric acids are qualitatively identical with the curves representing the variation of the velocity of the cathodic evolution of hydrogen with the concentration of the same acids.

3. The data in the papers by Z. Iofa and A. Frumkin on the hydrogen overvoltage at mercury and lead cathodes in hydrochloric and sulfuric acids and the data on the equilibrium hydrogen-electrode potential in these same solutions have been used to show that the rates of chromium and iron dissolution and the velocity of the cathodic evolution of hydrogen at a lead cathode vary identically, within the limits of experimental error, as the concentration of sulfuric acid is raised. In the case of hydrochloric acid, the velocity of the cathodic process rises faster than the rates of metal dissolution as the acid concentration is increased.

4. It has been shown that these behavior patterns are in good agreement with Z. Iofa's and A. Frumkin's theory of hydrogen overvoltage in concentrated acids.

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*See Consultants Bureau English Translation page a-605.
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COMPLEX FLUORINE - TITANIUM IONS IN SOLUTION

K. E. Kleiner

Reactions involving the decolorization of solutions of colored compounds of some metals by fluorine ions are employed, as we know, in the colorimetric determination of fluoride concentrations; all the methods based upon these reactions have been elaborated empirically, however, so that the field of their application has been limited by the close confines of the concrete problem for which the given method of analyzing a given object has been developed.

To extend the limits of application of these methods and to secure comparative indexes for each of them, we first have to make a study of the equilibria that control the decolorizing action of fluorine ions.

The most important of these equilibria are the following:

$$MeX_m^{\alpha-m\beta} + nF^- \rightleftharpoons MeF_n^{\alpha-n} + mX^{\beta} \qquad (I)$$

$$MeF_n^{\alpha-n} \rightleftharpoons Me^{\alpha} + nF^- \qquad (II)$$

$$MeX_m^{\alpha-m\beta} \rightleftharpoons Me^{\alpha} + mX^{\beta} \qquad (III)$$

where $MeX_m^{\alpha-m\beta}$ is the colored metal compound, and X is the anion of the acid or the electrically neutral molecule (such as H_2O_2).

Equilibrium (I) is obviously determined not only by the activities of the reagents, but mainly by the stability relations, i.e., by the magnitudes of the instability constants of the compounds $MeF_n^{\alpha-n}$ and $MeX_m^{\alpha-m\beta}$ which are governed by Equilibria (II) and (III).

Hence, a study of Equilibria (II) and (III) must precede any endeavor to perfect present methods of determining fluorides or of developing new ones, not merely empirically, but guided by definite laws. The reaction between a solution of a titanium peroxide compound and fluorides is a special example of Equilibrium (I).

Numerous papers have been published on the behavior of peroxide compounds of titanium and other metals in solution [Equilibrium (III)]. They include papers by M. Rumpf [1], M. Bendig and H. Hirschmuller [2], and A.K. Babko and A.I. Volkova [3]. The last-named authors have shown that there are two compounds of titanium with hydrogen peroxide. In acid solutions (at a pH less than 2) a colored addition product of a molecule of hydrogen peroxide and ions of titanium or titanyl are formed. When the pH exceeds 3, a colorless salt-like compound is formed with anions of hydrogen peroxide (HO_2^- or O_2^{--}) in the coordination sphere. Only the colored compounds are of any use in colorimetric determination of the fluorides, of course.

These authors found that the hydrogen peroxide molecules enter into the complex ions of the colored compound in the same proportions as the titanium or titanyl ions, so that the constit of the complex ions may be represented by the formula $TiH_2O_2^{4+}$ or $TiOH_2O_2^{2+}$

The instability constant of this compound when dissociated is as follows:

$$TiH_2O_2^{4+} \rightleftharpoons Ti^{4+} + H_2O_2,$$

$$TiOH_2O_2^{2+} \rightleftharpoons Ti^{2+} + H_2O_2,$$

averages $1 \cdot 10^{-4}$, according to the authors cited [1, 2, 3].

Though many fluorine compounds of titanium have been described in the literature, no research has been done on the constitution and stability of these compounds in solution [Equilibrium (II) in the foregoing outline].

It is only in the paper by M. Bendig and H. Hirschmuller [2] that we can find indirect evidence of the stability of coordination compounds of titanium and fluorine; these authors determined the equilibrium constant of the reaction between a titanium compound and sodium fluoride in aqueous solution, finding $K_{equil.} = 3.5 \cdot 10^{-3}$.

In the present paper we report the results of an experimental determination of the composition and stability of fluoride complex ions of titanium, secured in an investigation of the $Ti(NO_3)_4$ [or $Ti(SO_4)_2$]-H_2O_2-NaF system in solutions of nitric and sulfuric acids.

All the experiments involved measurements of the optical density of the solutions in a Pulfrich photometer with a No. 7 light filter (effective wavelength 465 mμ). The initial solution of titanium nitrate was prepared from the sulfate by precipitating the hydroxide three times and dissolving it in nitric acid. The titanium concentration of the solution was determined gravimetrically. The solution of sodium fluoride was prepared with the calculated quantity of the refined preparation, while the concentration of hydrogen peroxide in the original solution was determined by permanganometry. The experimental procedure and the computations were exactly like those employed in the research on fluorine coordination compounds of iron in solution [4].

The Composition of a Fluorine Coordination Compound of Titanium in Solution. The composition was determined in solutions in sulfuric and nitric acids by means of a restricted logarithmic method [5] and by the Job method [6,7].

The results obtained with the restricted logarithmic method for sulfuric-acid solutions (0.5N H_2SO_4) with a titanium concentration of $45.0 \cdot 10^{-3}$ mol per liter and a hydrogen-peroxide concentration of $85 \cdot 10^{-3}$ mol per liter are given in Table 1 and Fig. 1. The concentration of sodium fluoride is given in Column 2. The cell thickness was 0.5 mm.

The results obtained in our tests of other solutions are illustrated in Figs. 2 and 3.

The experimental figures obtained when the sulfuric-acid solutions were mixed (as in the Job method) are shown in Figs. 4 and 5. Curve 6 in these figures represents the change in the optical density of the solutions containing titanium, hydrogen peroxide, and sodium fluoride with variations in the ratio F/Ti, plotted along the axis of abscissas. The optical density of the solutions that contain nothing but titanium and hydrogen peroxide (in the same concentrations as for the Curves b) is represented by Curves a. The c curves were plotted from the difference between the optical densities of the a and b solutions; they indicate the progress of decolorization of the solutions ($\bar{D}$ ordinate), i.e., the change in the concentration of the fluorine coordination compound of titanium as a function of the F/Ti ratio.

These results show that the maximum decolorization of the solutions, i.e., the maximum formation of the coordination compound of titanium and fluorine, occurs at the ratio F:Ti=1:1.

Curves 1 and 2 in Figs. 1 and 3 have been constructed on the assumption that in the formula TiF_n^{4-n}, n = 1 and 2. Experimental data shown as circles in these figures agree well with the curves calculated for n = 1.

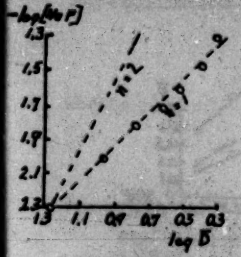

Fig. 1. Sulfuric-acid solutions (0.5N H_2SO_4). $[Ti(SO_4)_2] = 45.0 \cdot 10^{-3}$; $[H_2O_2] = 85 \cdot 10^{-3}$ mol/liter. Cell thickness 0.5 mm.

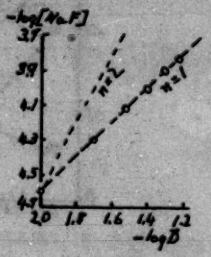

Fig. 2. Nitric-acid solutions (0.1N HNO_3). $[Ti(NO_3)_4] = 4.93 \cdot 10^{-3}$; $[H_2O_2] = 9.24 \cdot 10^{-3}$ mol/liter. Cell thickness 1 mm.

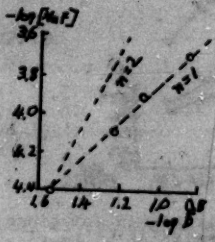

Fig. 3. Nitric-acid solutions (0.1N HNO_3). $[Ti(NO_3)_4] = 0.73 \cdot 10^{-3}$; $[H_2O_2]$ $0.78 \cdot 10^{-3}$ mol/liter. Cell thickness 50 mm.

Table 1

Test No.	NaF concentration, mol /liter	Optical density $\log \frac{I_o}{I}$	Weakening of the color, $\bar{D}$	$-\log \bar{D}$	$-\log [NaF]$
1	-	1.04	-	-	-
2	0.005	0.985	0.055	1.26	2.3
3	0.01	0.93	0.11	0.96	2.00
4	0.015	0.87	0.17	0.77	1.82
5	0.02	0.80	0.24	0.62	1.70
6	0.025	0.74	0.30	0.52	1.60
7	0.035	0.63	0.41	0.39	1.46
8	0.05	0.55	0.49	0.31	1.30

It follows from the experiments using the restricted logarithmic method and the Job method, therefore, that at the concentrations cited above (Table 1 and Figs. 1-5) fluorine and titanium enter complex ions in a 1 : 1 ratio, so that the composition of the latter may be represented by TiF^{3+} or $TiOF^{+}$.

The question whether a fluorine compound of titanium contains a titanium or titanyl ion cannot be answered by this investigation. Some of the experimental findings obtained in our determinations of composition and of the instability constant (vide infra) suggest that the formula $TiOF^{+}$ is to be preferred. By employing the functions derived by A.K. Babko [8, 9] the instability constants of more complicated ions may be calculated from the instability constants of a complex ion containing a single coordinated ion. This has been demonstrated in a number of papers, particularly in research on complex ions of fluorine with iron [4], aluminum [10], and beryllium [11]. These relationships hold good only for complex ions in which the charge on the central ion is neither screened nor neutralized (even if only partially) by other molecules or ions. A calculation for complex ions of fluorine and titanium has shown that we might expect the formation of a perceptible concentration (and at a certain composition an appreciable) concentration of complex ions with two coordinated ions of fluorine.

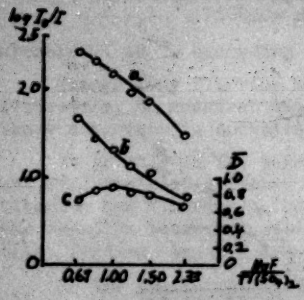

Fig. 4. Sulfuric-acid solutions (1N H_2SO_4). $[Ti(SO_4)_2]$ + [NaF] = 0.015 mol/liter. $[H_2O_2]$ = 0.075 mol/liter. Cell thickness 10 mm.

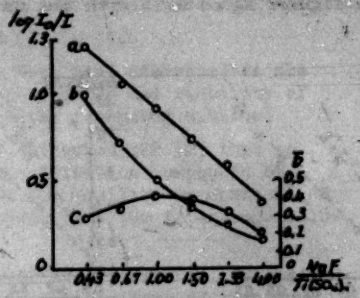

Fig. 5. Sulfuric-acid solutions (2N H_2SO_4). $[Ti(SO_4)_2]$ + [NaF] = 0.15 mol/liter. $[H_2O_2]$ = 0.26 mol/liter. Cell thickness 0.25 mm.

Inasmuch as this has not been supported experimentally, it may be concluded that the addition of a second fluorine ion involves the expenditure of considerable energy, as would follow from the functions referred to, so that we may assume that other ions than those of titanium and fluorine participate in the formation of the coordination compounds. We shall therefore prefer henceforth to represent the composition of the complex ions of fluorine and titanium by the formula $TiOF^+$, without regarding it as an established fact (this applies equally to the peroxide compound of titanium: $TiOH_2O_2^{2+}$).

In accordance with present concepts the titanium ion can move about within the oxygen octahedron inside which it is located in the space lattice of barium titanate, which is, as we know, a new Seignetto-electric. The bond between the titanium ion and the oxygen ions is partially homopolar, so that the titanium ion is displaced some 0.1 Å from the center of the octahedron toward one of the 6 adjacent oxygen ions. Inasmuch as Seignetto electric properties have been discovered in other titanates of divalent metals [12], it may be assumed that the asymmetrical arrangement of the titanium and oxygen ions is a general property of complex titanium ions containing oxygen. We may, therefore, expect that in these complex ions the bond between the titanium ion and one of oxygen ions surrounding it will be stronger than its bond with the other oxygen ions.

This bond apparently persists even in solution (titanyl ions).

Instability Constant of Complex Ions of Fluorine and Titanium

To determine the instability constant

$$K_{TiOF^+} = \frac{[TiO^{2+}]\,[F^-]}{[TiOF^+]}$$

we ran a series of tests in 0.1N solutions of nitric acid under conditions resembling those used in determining the instability constants of FeF^{2+} and other complex ions [4, 10, 11].

The reaction involved in the decolorization of a peroxide compound of Ti n by fluorine ions is given by the underlying equilibrium:

$$TiOH_2O_2^{2+} + F^- \rightleftharpoons TiOF^+ + H_2O_2.$$

The equilibrium constant is:

$$K_{equil.} = \frac{[TiOF^+][H_2O_2]}{[TiOH_2O_2^{2+}][F^-]} = \frac{K_{TiOH_2O_2^{2+}}}{K_{TiOF^+}},$$

whence

$$K_{TiOF^+} = K_{TiOH_2O_2^{2+}} \frac{[TiOH_2O_2^{2+}][F^-]}{[TiOF^+][H_2O_2]},$$

where $K_{TiOH_2O_2^{2+}} = 1 \cdot 10^{-4}$.

The equilibrium concentration $TiOH_2O_2^{2+}$ in solutions containing a fluoride was determined experimentally from the changes in the optical density of these solutions (cols. 5, 6, and 7 in Table 2).*

The equilibrium concentrations of TiO^{2+}, $TiOF^+$, and F^- were calculated as follows. The concentration of TiO^{2+} was calculated from the expression for $K_{TiOH_2O_2^{2+}}$ after computing the equilibrium concentration of the hydrogen peroxide from $[H_2O_2]_{equil.} = [H_2O_2]_{tot.} - [TiOH_2O_2^{2+}]$.

The $TiOF^+$ concentration was calculated from the equation $[TiO(NO_3)_2] = [TiO^{2+}] + [TiOH_2O_2^{2+}] + [TiOF^+]$, while the equilibrium concentrations of the fluorine ions were calculated from the expression $[NaF] = [TiOF^+] + [HF] + [F^-]$, bearing in mind [13] that

$$K_{HF} = \frac{[H^+][F^-]}{[HF]} = 10^{-3}$$

All the experimental and computational data are listed in Table 2. All the concentrations are stated in mols or gram-ions per liter. The cell thickness was 50 mm. The instability constants of the complex ions TiOF are tabulated in Col. 11. We took the mean value of 19 tests to be $K_{TiOF^+} = 3.6 \cdot 10^{-7}$ the values ranging from $1.8 \cdot 10^{-7}$ to $4.7 \cdot 10^{-7}$.

As has been stated above, all the determinations of the instability constant were made in 0.1N solutions of nitric acid.

The equilibrium constant is:

$$TiOF^+ + H_2O_2 \rightleftharpoons TiOH_2O_2^{2+} + F^-$$

$$K_{equil.} = \frac{[TiOH_2O_2^{2+}][F^-]}{[TiOF^+][H_2O_2]} = \frac{K_{TiOF^+}}{K_{TiOH_2O_2^{2+}}} = \frac{3.6 \cdot 10^{-7}}{1 \cdot 10^{-4}} = 3.6 \cdot 10^{-3}.$$

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*The concentration of $TiOH_2O_2^{2+}$ in solutions that contain no NaF may be readily computed from the equation:

$$K_{TiOH_2O_2^{2+}} = \frac{([TiO(NO_3)_2] - [TiOH_2O_2^{2+}])([H_2O_2] - [TiOH_2O_2^{2+}])}{[TiOH_2O_2^{2+}]} = 1 \cdot 10^{-4}$$

TABLE 2

No.	$[Ti(NO_3)_4]\cdot10^5$	$[H_2O_2]\cdot10^5$	$[NaF]\cdot10^5$	$\log \frac{I_0}{I}$	$\frac{\log \frac{I_x}{I}}{\log \frac{I_0}{I}}$	$[TiO(H_2O_2)]\cdot10^5$	$[TiO^{2+}]\cdot10^5$	$[TiOF^+]\cdot10^5$	$[F^-]\cdot10^6$	$K_{TiOF^+}\cdot10^7$
1	2	3	4	5	6	7	8	9	10	11
1	54.56	95.00	-	0.78	1	45.39	-	-	-	-
2	54.56	95.00	5	0.73	0.94	42.67	8.15	3.74	0.13	2.8
3	54.56	95.00	10	0.68	0.87	39.49	7.11	7.96	0.20	1.8
4	54.56	95.00	15	0.66	0.85	38.58	6.84	9.14	0.39	4.4
5	54.56	95.00	20	0.63	0.81	36.76	6.31	11.49	0.85	4.7
6	54.56	95.00	25	0.60	0.77	34.95	5.82	13.79	1.12	4.7
7	54.56	95.00	30	0.57	0.73	33.13	5.36	16.07	1.39	4.6
8	54.56	139.88	-	0.85	1	49.14	-	-	-	-
9	54.56	139.88	5	0.81	0.95	46.68	5.01	2.87	0.21	3.7
10	54.56	139.88	10	0.77	0.91	44.72	4.70	5.14	0.49	4.4
11	54.56	139.88	15	0.71	0.84	41.28	4.19	9.09	0.59	2.7
12	54.56	139.88	20	0.69	0.81	39.80	3.98	10.78	0.92	3.4
13	54.56	139.88	25	0.66	0.78	38.33	3.77	12.46	1.25	3.8
14	54.56	139.88	30	0.64	0.75	36.86	3.58	14.12	1.59	4.0
15	54.56	139.88	35	0.60	0.71	34.88	3.32	16.36	1.86	3.8
16	54.56	186.5	-	0.88	1	50.81	-	-	-	-
17	54.56	186.5	10	0.78	0.89	45.22	3.20	6.14	0.39	2.0
18	54.56	186.5	20	0.73	0.83	42.17	2.92	9.47	1.05	3.2
19	72.75	97.88	-	1.07	1	58.13	-	-	-	-
20	72.75	97.88	20	0.87	0.81	47.08	9.27	16.40	0.36	2.0
21	72.75	97.88	25	0.85	0.79	45.92	8.84	17.99	0.70	3.4
22	72.75	97.88	30	0.81	0.76	44.18	8.23	20.34	0.97	3.9
23	72.75	97.88	35	0.78	0.73	42.43	7.65	22.67	1.23	4.2

Average ... $3.6\cdot10^{-7}$

This value agrees satisfactorily with the value of the constant ($K_{equil.}=3.5\cdot10^{-3}$) given by other authors [2]. This agreement serves as indirect proof that we have determined the value of the instability constant of complex ions of fluorine and titanium correctly.

SUMMARY

1. It has been found that the composition of a complex ion of fluorine and titanium in solutions of nitric and sulfuric acids is given by the ratio F:Ti = 1:1 for concentrations of sodium fluoride ranging from $2.5\cdot10^{-5}$ to 0.12 mol per liter.

It is assumed that under these conditions titanyl ions participate in the formation of complex ions, so that the composition of the complex ions may be represented by the formula $TiOF^+$.

2. The instability constant of the complex ions $TiOF^+$ has been determined to be:

$$K_{TiOF^+} \frac{[TiO^{2+}][F^-]}{[TiOF^+]} = 3.6 \cdot 10^{-7}.$$

3. The equilibrium constant of $TiOF^+ + H_2O_2 \rightleftharpoons TiOH_2O_2^{2+} + F^-$ has been calculated as:

$$K_{equil.} = 3.6 \cdot 10^{-3}.$$

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DOUBLE DECOMPOSITION IN THE ABSENCE OF A SOLVENT

THE FORMATION OF COORDINATION COMPOUNDS, SOLID SOLUTIONS, AND DOUBLE DECOMPOSITION IN MOLTEN CALCIUM AND STRONTIUM FLUORIDES AND CHLORIDES.

G. A. Bukhalova and A. G. Bergman

Research on double decomposition in molten salts is even more interesting when investigating various systems possessing cations or anions in common. In such a case we observe evolution of the diagram, as one set of ions is replaced by another. In research on various fluoride-chloride systems of the alkali-earth elements Ca, Sr ‖ F, Cl (of the present paper); Ca, Ba ‖ F, Cl [1], and Sr, Ba ‖ F, Cl [2], for instance, we can establish the effect of various factors, such as: the radius of the cation, the nominal thermal effect of the exchange reaction, the formation of coordination compounds, and the like, upon the double decomposition and the progressive change in the structural diagram as the system's cations are changed.

Investigation of fluoride-chloride exchange is valuable because systems consisting of fluorides and chlorides are comparatively simple, inasmuch as: 1) they exhibit only a slight tendency to form solid solutions; 2) their fusion curves are usually very steep and intersect sharply; 3) up to the present time no instance has been found of the crystallization of binary or ternary heterogeneous compounds from the melts of any interhalogen reciprocal system; and 4) another favorable factor is the circumstance that all the halogen compounds crystallize readily and have the simplest constitutions.

We shall reserve consideration of the general nature of the Ca, Sr ‖ F,Cl system we have investigated for our conclusions, where we consider it together with other fluoride-chloride systems of the alkali-earth metals and make a comparative analysis of these systems and discuss them.

Here we shall merely state that the diagram of the crystallization surface of the Ca, Sr ‖ F, Cl system consists of three areas of continuous series of solid solutions of fluorides of Ca and Sr, chlorides of Ca and Sr, and the compounds CaF_2CaCl_2 and $SrF_2 \cdot SrCl_2$ (Fig.1).

EXPERIMENTAL

Procedure

The research was carried out by the visual polythermal method in a platinum crucible. Temperatures were measured with a Pt-PtRh thermocouple and a Siemens-Halske mirror galvanometer. The melts were vigorously stirred by hand with a platinum stirrer throughout the process of slow cooling until crystals appeared in the molten mass, and, conversely, throughout the slow heating until all the crystals disappeared. The interior of the electric

furnace was illuminated by a powerful light source to obliterate the light emitted by the molten salts. The initial calcium and strontium chlorides, marked "chemically pure," were recrystallized twice from water; the calcium and strontium fluorides were prepared by dissolving the respective carbonates (prepared in turn from the doubly recrystallized chlorides and ammonium carbonate) in hydrofluoric acid that had been twice distilled in a platinum still.

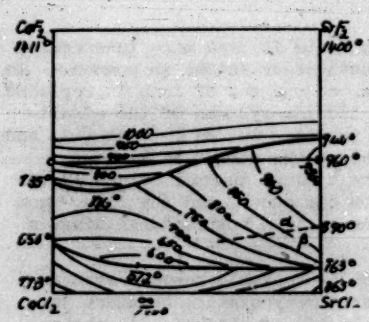

Fig. 1. Projection of the polytherm of the reciprocal Ca, Sr || F, Cl system.

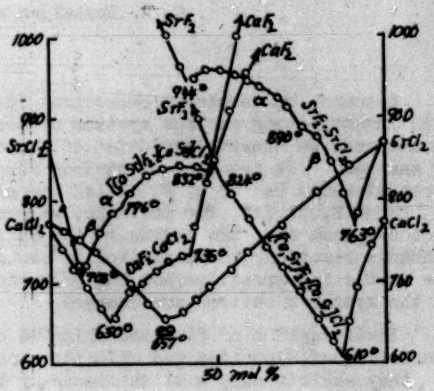

Fig. 2. Fusion curves of binary systems and diagonal sections.

The melting points of the initial substances were as follows: $CaCl_2$-773°, $SrCl_2$-868°, CaF_2-1411°, and SrF_2-1400° (the latter two figures were not measured). $SrCl_2$ exhibits several homeomorphic transformations at 818, 725, and 630°, while $CaCl_2$ has one at 608°. These homeomorphic transformations of the $SrCl_2$ and $CaCl_2$ salts are not manifested in the system under investigation, as their temperatures lie below the fusion curve.

The experimental investigations were continued up to 1000°. All compositions are stated in molecular per cent.

Lateral Sides-Binary Systems (Fig. 2, Table 1)

1. CaF_2-$CaCl_2$ has been investigated by Nacken [3] and Plato [4], who found that a 1 : 1 incongruent compound was formed. We repeated their work on this system. The eutectic point lies at 650° and 19.0% CaF_2, the transition point being located at 735° and 42.5% CaF_2.

TABLE 1

CaF_2-$CaCl_2$		SrF_2-$SrCl_2$		$SrCl_2$-$CaCl_2$		$SrCl_2$-CaF_2		$CaCl_2$-SrF_2	
Mol.% CaF_2	t°	Mol.% SrF_2	t°	Mol.% $SrCl_2$	t°	Mol.% CaF_2	t°	Mol.% SrF_2	t°
0	773	0	868	0	773	0	868	0	773
4	742	8	784	5	764	4	795	4	746
8	720	12	806	10	753	8	751	8	693
12	696	16	846	15	739	12	723	12	651
20	658	20	877	20	715	16	762	16	627
24	687	24	888	25	697	20	785	20	653
28	700	28	913	30	675	25	809	25	687
32	713	32	924	35	656	30	830	30	617
36	725	36	937	40	665	35	838	35	742
40	730	40	944	44	679	40	842	40	776
44	788	44	948	48	697	45	840	45	807
47	820	48	958	55	716	50	843	50	848
57	1000	52	958	60	736	55	907	55	900
		56	950	70	770	60	954		
		60	963	80	808				
		64	1000	90	840				
				100	868				
Intersection: 1) 650° and 19% CaF_2, 2) 735° and 42.5% CaF_2		Intersection: 1) 736° and 14% SrF_2, 2) 890° and 25.05% SrF_2; 3) 944° and 58% SrF_2		Minimum: 656° and 35% $SrCl_2$		Intersection: 1) 708° and 10% CaF_2, 2) 796° and 23% CaF_2, 3) 832° and 49% CaF_2		Intersection: 1) 610° and 13% SrF_2, 2) 824° and 48% SrF_2	

2. SrF_2-$SrCl_2$ has been investigated by Plato [4] and by Vinter [5], who found the congruent compound $SrF_2 \cdot SrCl_2$. Our checks of this diagram indicate that our findings do not differ essentially from those given by Plato, except for the presence of a $SrF_2 \cdot SrCl_2$ homeomorphic transformation at 890°° and 25% SrF_2.

We have found that the melting point of $SrF_2 \cdot SrCl_2$ is 960°, with its first eutectic at 763° and 14% SrF_2 and its second at 944° and 58% SrF_2.

3. We did not do any research on CaF_2-SrF_2, owing to the high temperatures involved; it must be supposed that the curve represents continuous solid solutions with a slight minimum, since we found continuous solid and a deep minimum at 1022° in the analogous system CaF_2-BaF_2, which we did not investigate. This is supported by the fact that the difference between the ionic radii of strontium and calcium is less than between those of barium and calcium (ionic radii: Ca - 1.06 A, Sr - 1.27 A, Ba - 1.43 A).

4. $CaCl_2$-$SrCl_2$ has been investigated by several authors [6,7,8]. We have found the minimum on the continuous fusion curve for the solid solutions to lie at 656° and 35% $SrCl_2$.

The reciprocal system Ca,Sr || F,Cl. Four internal and two diagonal sections were passed through this system to map the relief of the crystallization surface. They are shown in Figs. 2 and 3 and in Tables 1 and 2, their location in the system being represented in Fig. 4. It should be noticed that the Sections I, II, and III and the diagonals $CaCl_2$-SrF_2 and $SrCl_2$-CaF_2 each consist of three crystallization branches, for they intersect three series of continuous solid solutions: strontium and calcium chlorides, the anionic complex ions of strontium and calcium, and finally, strontium and calcium fluorides, denoted in the drawings as [Ca, Sr]Cl_2, [Ca, Sr]F_2·[Ca, Sr]Cl_2 and [Ca,Sr]F_2.

The homeomorphic transformations, which are so readily observable in the SrF_2-$SrCl_2$ binary system along the branch representing the $SrF_2 \cdot SrCl_2$, compound, were followed by us only along Section I and the $SrCl_2$-CaF_2 diagonal. Section IV consists of a single branch, inasmuch as all of it lies within the region representing solid solutions.

In Fig. 5 we also show the projection of the line of joint crystallization upon the $CaCl_2$-$SrCl_2$ side, which we used to find the isothermal points on the joint crystallization lines, to fix more accurately the location of the minima on these lines, and to estimate the correspondence of the sections.

Inspecting the projection of the system's liquidus (Fig.1) and the projection of the line of joint crystallization upon the $CaCl_2$-$SrCl_2$ side (Fig.5), we conclude that the crystallization surface of the system consists of three crystallization areas, separated by two boundary curves possessing minima; they separate the crystallization area of a continuous series of solid solutions of the compounds [Ca,Sr]F_2·[Ca,Sr]Cl_2 from the areas representing the continuous series of solid solutions of calcium and strontium chlorides and calcium and strontium fluorides. The area of the composition square is allocated as follows among the three crystallization areas: 52.68% [Ca,Sr]F_2; 36.28% [Ca,Sr]F_2·[Ca,Sr]Cl_2; and 11.04% [Ca,Sr]Cl_2. It should be borne in mind that the crystallization surface of the solid solutions of the compounds [Ca,Sr]F_2·[Ca,Sr]Cl_2 is shown as a bent truncated cone on the projection of the liquidus diagram expanding from $CaF_2 \cdot CaCl_2$ to $SrF_2 \cdot SrCl_2$.

TABLE 2

Section I: 55% $SrCl_2$, 45% $CaCl_2$ } SrF_2

Mol.% SrF_2	t°
0	716
2	690
4	660
6	643
8	622
10	644
11	663
17	725
22	771
27	806
32	839
42	881
47	896
52	906
57	918
64	1002

Intersection:
1) 615° and 9% SrF_2,
2) 754° and 21% SrF_2,
3) 914° and 51.5% SrF_2

Section II: 50% $SrCl_2$, 50% $CaCl_2$ } CaF_2

Mol.% CaF_2	t°
0	685
3	642
6	611
9	576
12	598
17	644
22	679
27	699
32	716
37	732
42	771
47	833

Intersection:
1) 565° and 10% CaF_2,
2) 738° and 39.5% CaF_2

Section III: 25% $SrCl_2$, 75% $CaCl_2$ } CaF_2

Mol.% CaF_2	t°
0	698
4	666
8	624
12	595
16	618
20	656
25	680
30	696
35	710
40	733

Intersection:
1) 581° and 12% CaF_2,
2) 716° and 39% CaF_2

Section IV: 25% CaF_2, 75% $CaCl_2$ } SrF_2: $SrCl_2$

Mol.% SrF_2 : $SrCl_2$	t°
0	677
10	685
15	689
20	698
24	705
28	711
31	719
34	725
37	735
40	747
44	763
48	778
52	797
60	830

The curve has no minimum

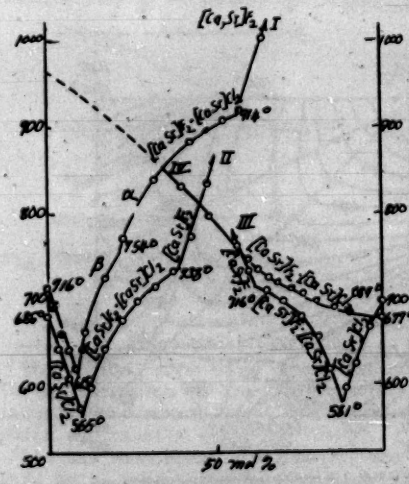

Fig. 3. Internal sections I, II, III, and IV of the system.

The isothermal lines plotted at intervals of 50° enable us to visualize the three-dimensional model of the Ca,Sr ‖ F,Cl system. It is quite obvious that in three dimensions the area of solid solutions of the compounds will be somewhat saddle-shaped.

Conclusion

The Ca,Sr ‖ F,Cl system brings the series of investigated reciprocal systems of fluorides and chlorides of the alkali-earth metals calcium, strontium, and barium to a close.

Three factors are strikingly exhibited in these systems: the formation of coordination compounds, double decomposition, and the stability of the solid solutions.

What is most characteristic of this series of systems: Ca,Sr ‖ F,Cl (Fig.1); Sr,Ba ‖ F,Cl (Fig.6); and Ca,Ba ‖ F,Cl (Fig.7) is the formation of coordination compounds at opposite sides, giving rise to fluorides and chlorides of the alkali-earth metals.

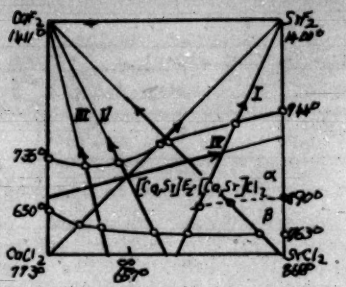

Fig. 4. Location of the system's internal sections.

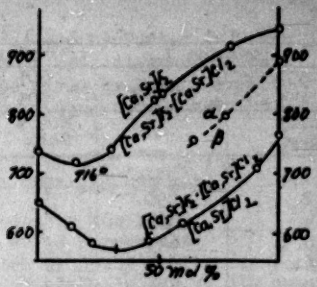

Fig. 5. Projection of the line of joint crystallization upon the $CaCl_2$-$SrCl_2$ side.

The stability of the resultant anionic coordination compounds increases with atomic number and ionic radius from calcium to barium. This is shown mainly by the melting points and heats of formation; the latter quantities were determined by N.K. Voskresenskaya and G.A. Bukhalova [10] for barium and strontium anionic coordination compounds, the data being expressed in large calories

TABLE 3

Coordination compound	Melting point	Kind of fusion	Heat of formation	
			From the Salts	From the elements
$BaF_2 \cdot BaCl_2$	1008°	Congruent . .	15.2	493.18
$SrF_2 \cdot SrCl_2$	960	Congruent . .	11.1	486.87
$CaF_2 \cdot CaCl_2$	735	Incongruent .	-	-

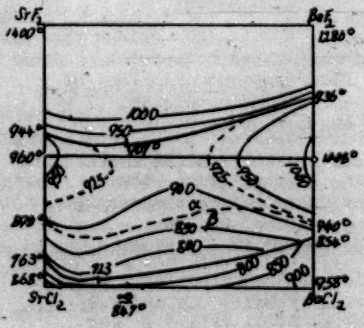

Fig. 6. Projection of the polytherm of the SrBa,‖F, Cl reciprocal system.

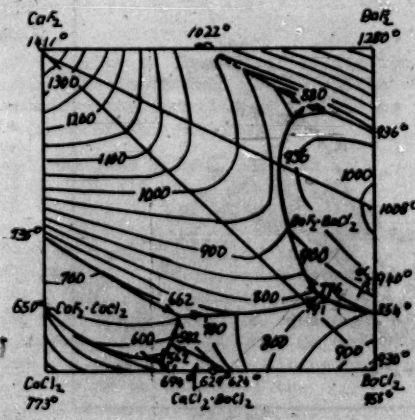

Fig. 7. Projection of the polytherm of the Ca,Ba‖ F,Cl reciprocal system.

The length of the crystallization branches of the compounds in the projections of the binary systems is 55, 50, and 23%, respectively.

In the chlorides, the formation of coordination compounds has been observed only between $CaCl_2$ and $BaCl_2$ as a coordination compound congruently fusing at 629°. Nor have coordination compounds containing four different ions, i.e., coordination compounds along the stable diagonals, been found.

If compounds are formed in the binary systems that bound the composition square, it is quite natural that the compound must manifest itself in some way or another in the reciprocal system, i.e., it must have a corresponding area in the diagram that represents the crystallization surface. Then a reaction involving the formation of the compound, i.e., the reaction involved in the formation of a coordination compound, will take place in the reciprocal system, in addition to a double decomposition reaction. Experiment has shown that the reactions involved in the formation of a coordination compound and in double decomposition are antagonistic ones in reciprocal systems.

This is clearly reflected in the liquidus diagrams of the reciprocal systems. Which one of these factors, double decomposition or the formation of a coordination compound, will prevail depends upon the nominal thermal effects of the respective reactions.* It is apparent that it would be more correct to employ the free energies rather than the heats of double decomposition and of the formation of coordination compounds. But it is only for very few systems that we are able to calculate the free energies of reactions, owing to the lack of the required constants. We therefore have to resort to the simplified nominal thermochemical effect of the reactions. But, as N. K. Voskresenskaya has shown [9], this simplification is quite permissible without impairing the correctness or the significance of the calculation. We have been able to calculate the double decomposition reactions and the reactions involved in the formation of coordination compounds for the Sr,Ba‖F,Cl system (Fig.6), i.e., to locate the triangulating secants of the system.**

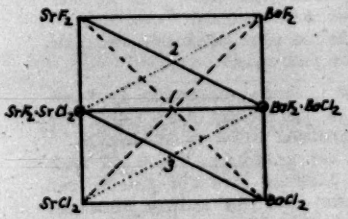

Fig. 8 Triangulation diagram of the Sr,Ba‖F,Cl system.

Fig. 8 is a diagrammatic sketch of the composition square of this system, with all possible sections shown. The equation for the reactions at the Point 1, where the sections of the square intersect, are represented as follows:

$$2SrCl_2+2BaF_2=2SrF_2+2BaCl_2+16.89 \text{ kcal.}$$
$$2SrF_2+2BaCl_2=SrF_2\cdot SrCl_2+BaF_2\cdot BaCl_2+17.79 \text{ kcal.}$$
$$2SrCl_2+2BaF_2=SrF_2\cdot SrCl_2+BaF_2\cdot BaCl_2+24.68 \text{ kcal.}$$

The reactions resulting in the formation of compounds entail greater thermal effects than do the double decomposition reactions. Therefore, when equimolecular proportions of

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*The thermal effects of double decomposition reactions and the reactions involved in the formation of coordination compounds are called nominal because they are calculated from the heats of formation of the constituent salts and the compounds, which are usually given for 18-25°.

**As has been pointed out above, the heats of formation of $SrF_2\cdot SrCl_2$ and $BaF_2\cdot BaCl_2$ were determined by N. K. Voskresenskaya and G.A. Bukhalova, which has made it possible for us to perform the computation cited here.

stable and unstable pairs of components are melted together, the compounds $SrF_2 \cdot SrCl_2$ and $BaF_2 \cdot BaCl_2$ must be formed. The predominance of the reactions involved in the formation of coordination compounds is expressed geometrically by the transverse cross section $SrF_2 \cdot SrCl_2$-$BaF_2 \cdot BaCl_2$ looking like a binary system, with a three-dimensional fold of maxima in the area corresponding to the solid solutions $[Sr,Ba]F_2 \cdot [Sr,Ba]Cl_2$. The diagonal section SrF_2-$BaCl_2$, representing the double decomposition reaction is not represented geometrically in the composition diagram by anything at all.

The $SrF_2 \cdot SrCl_2$-$BaF_2 \cdot BaCl_2$ section divides the composition square into two tetragons: I) $SrF_2 \cdot SrCl_2$-$BaF_2 \cdot BaCl_2$-BaF_2-SrF_2 and II) $SrF_2 \cdot SrCl_2$-$BaF_2 \cdot BaCl_2$-$BaCl_2$-$SrCl_2$. In turn, each of these tetragons may be regarded as an independent reciprocal system, which may be triangulated in turn. In Tetragon I the reaction at Point 2 is the controlling one:

$$2BaF_2+SrF_2 \cdot SrCl=BaF_2 \cdot BaCl_2+2SrF_2+1261 \text{ kcal.}$$

the reaction at Point 3 controlling in the Tetragon II:

$$2SrCl_2+BaF_2 \cdot BaCl_2= SrF_2 \cdot SrCl_2+2BaCl_2+4.41 \text{ kcal.}$$

We have been unable to perform a complete calculation of all the triangulating secants in the Ca,Sr ‖ F,Cl and Ca,Ba ‖ F,Cl systems, i.e., all the possible reactions occurring in these systems, because of the absence of data on the heat of formation of the coordination compound $CaF_2 \cdot CaCl_2$. As a result we cite merely our calculations of the nominal thermal effects of the double decomposition reaction:

$$CaCl_2+SrF_2=CaF_2+SrCl_2+8.47 \text{ kcal.}$$
$$CaCl_2+BaF_2=CaF_2+BaCl_2+16.98 \text{ kcal.}$$

Experience in research on reciprocal systems containing coordination compounds indicates that the formation of coordination compounds usually prevails over double decomposition in reversible-reciprocal systems.

This is manifested in the liquidus diagram by the coordination compounds having well-developed areas, while the secants originating at the point in the graph that represents the composition of the coordination compounds look like binary systems, and sometimes even make it impossible to plot diagonal secants, constituting so-called adiagonal reciprocal systems.

This behavior pattern is in conformity with the fluoride-chloride systems of the alkali-earth metals. As a matter of fact, in the Ca,Sr‖ F,Cl (Fig.1) and Sr,Ba‖ F,Cl (Fig.6) systems, where the nominal thermal effects of double decomposition are 8.44 and 8.47 kcal, respectively, per molecule, and 4.22 and 4.23 kcal, respectively per equivalent, the liquidus diagram (and for the Sr,Ba‖ F,Cl system, as we have seen, calculation also) shows that the stable sections in these systems are the transverse ones that connect the points representing the compositions of two coordination compounds together; they divide the composition square into two tetragons. The extreme anticlinal folds are located along the stable secants.

In the Ca,Ba‖ F,Cl system the nominal thermal effect of the double decomposition reaction is 16.98 kcal per molecule and 8.49 kcal per equivalent. The system is an irreversible-reciprocal one, so that the areas representing the compounds $CaF_2 \cdot CaCl_2$ and $BaF_2 \cdot BaCl_2$ are not interconnected, being separated by the stable diagonal CaF_2-$BaCl_2$.

As the liquidus diagram indicates (Fig.7), the areas of the two coordination compounds are forced back toward the sides by the ridge of the stable components. When equimolecular proportions of the coordination compounds are melted together, we get the components of the stable section:

$$CaF_2 \cdot CaCl_2+BaF_2 \cdot BaCl_2=2CaF_2+2BaCl_2.$$

As has been stated above, one of the characteristic features of these systems: CaSr ‖ F,Cl; Ca,Ba ‖ F,Cl; and Sr,Ba ‖ F,Cl is their tendency to form solid solutions.

We know that one of the prerequisites for the formation of solid solutions of two constituents that possess ionic lattices is that their ionic radii be as close together as possible. The difference between the ionic radii is 0.11 A for Sr-Ca, 0.16 A for Ba-Sr, and 0.37 A for Ba-Ca.

The large difference of 0.37 A between the ionic radii of Ca^{++} and Ba^{++} and the comparatively high thermochemical effect of the double decomposition reaction: 8.49 kcal per equivalent in the Ca,Ba ‖ F,Cl system hinders the formation of solid solutions of the compounds. On the other hand, the low thermal effects of the double decomposition reactions in the Ca,Sr ‖ F,Cl and Sr,Ba ‖ F,Cl systems are unable to counteract the tendency to form solid solutions of Ca-Sr and Sr-Ba chlorides and Ca-Sr and Sr-Ba fluorides, and of the corresponding coordination compounds.

SUMMARY

1. The fusion diagram of the Ca,Sr ‖ F,Cl system, consisting of the three crystallization surfaces of the solid solutions: Ca and Sr fluorides, Ca and Sr chlorides, and the two coordination compounds: the incongruently fusing compound, $CaF_2 \cdot CaCl_2$, and the congruently fusing compound $SrF_2 \cdot SrCl_2$, has been investigated by the visual-polythermal method.

2. The nominal thermochemical effect of the double decomposition reaction, totaling 4.23 kcal per equivalent on the CaF_2-$SrCl_2$ side, is unable to rupture the continuous series of solid solutions of the two coordination compounds, so that the reciprocal system's square is first divided into two tetragons, which can be triangulated still further, thus being divided into phase triangles.

3. The results of our researches on three reciprocal systems, constituted by the fluorides and chlorides of calcium, strontium, and barium are discussed, and the laws governing the formation of coordination compounds as against double decomposition are discussed.

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THE THERMAL EFFECT OF THE NATURAL AGING PROCESS IN AN Al-Cu ALLOY (5% Cu) AFTER HARDENING AND RECOVERY

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An alloy of Al with 5% Cu is a typical example of an alloy capable of aging (self-hardening) after being tempered.

Numerous papers have dealt with the mechanism involved in the processes that cause this alloy to harden as it ages. Historical surveys of the evolution of concepts regarding this process are to be found in the papers by S. T. Konobeyevsky [1] and D. A. Petrov [2].

The phenomenon of recovery, i.e., a sharp change in various properties of this alloy produced by a brief low-termperature annealing, has also engaged the attention of many researchers. D. A. Petrov [2] has made a thorough study of this problem. S. T. Konobeyevsky has proposed a thermodynamical theory of recovery [1]. The data in the literature and his own researches have led S. T. Konoveyevsky to conclude that even natural aging (that is, aging at room temperature) involves the separation from the supersaturated solid solution of a phase with the composition of Al_2Cu, very highly dispersed through the bulk of the supersaturated solid solution and in a state of metastable equilibrium with it. The phenomenon of recovery is attributed to the dissolution of this phase as the temperature is raised.

We know that the aging of alloys involves the evolution of heat. Swentoslawksi and Czochralski [3] and Czochralski, Smoluchowski, and Calus [4], for instance, have investigated the heat evolved in the aging of duraluminum. According to these authors, the process takes about 11 days, the heat evolved totaling 1.75 ± 0.05 cal/gram. The authors mention two more interesting facts: 1) the time curve of the evolution of heat exhibits a maximum, the location of this maximum depending upon the aging temperature; and 2) the kinetics of the evolution of heat changes markedly for even minute changes in the aging temperature (20 and 26°), though the total heat evolved (at 20 and 26°) remains the same.

An indirect criterion of the thermal effect of the aging of duraluminum may also be obtained from the Swindells and Sykes curves of the apparent heat capacity [5]. Comparing their findings for newly hardened and for aged duraluminum, these authors estimate the heat evolved in aging to approximate 1.4 cal/gram, which is rather close to the figure cited by Czochralski and his associates.

It is only in the paper by Calus and Smoluckowski [6] that we find any data on the heat evolved in the aging of binary Al-Cu alloys; stipulating that their data are merely preliminary, these authors give the following figures:

Per cent Cu in the alloys	1.48	2.82	4.18
Total head evolved during aging, cal/gram	0.057	0.092	0.290

The authors comment that the length of time during which heat is evolved increases with the percentage of copper, and that the process is concluded

within about 72 hours for 4.18% Cu. There is nothing at all in the literature on the heat evolved during aging of alloys after recovery.

The present paper represents an attempt to study the thermal effects involved in the natural aging of an Al-Cu alloy (5% Cu) during several consecutive hardening-aging cycles and after a short period of low-temperature annealing (recovery). We were interested in measuring not only the total heat evolved by the alloy, but also in securing data on the kinetics of the rate at which the heat was evolved.

Method. A sample of the alloy (about 17 grams) was kept in a furnace at constant temperature for some time, after which it was quenched in water at room temperature for 1 minute and transferred to a calorimeter. The calorimeter was a copper block (weighing some 500 grams), having a conical depression that exactly matched the shape of the sample. The experiments were run under adiabatic conditions, but the aging process may be regarded as isothermal, since the temperature rise did not exceed 0.2-0.3° in any test. The sensitivity of the calorimetric apparatus was such as to detect the evolution of 0.003 cal per gram of alloy. No higher sensitivity was required in this case, since the reproducibility of the thermal effect of aging in various samples of the alloy was of the same order of magnitude, as will be seen below. The heat losses of the calorimeter were carefully checked, making it possible to make measurements within 4 to 6 hours that yielded reliable results.

The fact that this calorimeter had often been employed in our laboratory for various researches and had been thoroughly tested was a guarantee that there were no appreciable systematic errors in the calometric measurements.

Some details of procedure. The samples were quenched in water as a rule. In only one test were the samples quenched in a large copper block (weighing about 10 kg) containing a recess to fit the sample. The temperature of the quenching bath was adjusted so as to bring the sample down to about the initial temperature of the calorimeter after 1 minute of quenching. The large amount of water used (about 10 liters) and its vigorous stirring ensured a practically constant water temperature during quenching ($\pm$0.2°). Quenching lasted 1 minute. Then the sample was wiped dry with filter paper as quickly as possible and transferred for 1-2 minutes to a thin-walled copper test tube immersed in the water enveloping the calorimeter. The temperature difference between the sample and the calorimeter was measured by a thermocouple, one junction of which was affixed to the sample, while the other was at the calorimeter's temperature. After the 1-2 minutes had elapsed, the sample was transferred to the calorimeter. This enabled correction for the heat introduced into the calorimeter by the sample owing to the difference in their temperatures. This correction was slight, its reliability being established by a long series of special tests. In these tests we checked whether the sample introduced enough moisture into the calorimeter to affect the calorimetric measurements. The temperature of the furnace used in the quenching tests was 520 + 2°, the samples being kept in the furnace for $1^1/_2$ hours. Longer soaking (3 hours) affected neither the total heat evolved during aging nor the kinetics of this evolution.

In our recovery tests the conditions (furnace temperature and soaking time) were chosen so as to have the sample give off the maximum quantity of heat as it aged. These optimum conditions (which were in full agreement with the findings of Petrov [2]) proved to be: a temperature of about 520° and a soaking time of 15 minutes. For some of the samples the measurements of the heat evolved were paralleled by Brinell hardness tests.

The evolution of heat by the sample was observed (by the calorimeter's rise in temperature) for several hours (4-6 hours in the tests after quenching and 2-3 hours in the tests after recovery). No longer observation was required, owing to the small amount of heat evolved, the total heat evolved by the sample being determinable with adequate accuracy by extrapolation from the experimental figures.

Samples. The alloy used in these tests was prepared from an aluminum 99.7% pure and electrolytic copper. Analysis indicated that the alloy contained 4.85% copper. The alloy was pressed into a bar, from which the samples were later turned. All the samples were annealed in vacuum as follows: 24 hours at 520° cooling for 51 hours at the rate of 7.7° per hour (down to 125°), and then cooling to room temperature at the rate of 15° per hour.

Test Results

a) Check of procedure.

Before commencing the experiments, we ran special tests to check our procedure. In these tests, instead of the alloy samples, samples made of pure aluminium, given the same preliminary treatment (heating in a furnace, quenching in water, drying, etc.), were placed in the calorimeter. These tests showed that the change in the calorimeter's temperature taking place after the sample had been placed within it was due solely to the difference between their temperatures. Heat transfer ended within 5-7 minutes, subsequent observation of the calorimeter temperature for several hours indicating that it remained quite constant.

b) Heat of aging after hardening.

The heat evolved during aging after hardening was measured at two temperatures (19.2 and 26.0°).

The results of these measurements are listed in Table 1 (for 19.2°) and Table 2 (for 26.0°).

These tables give the amount of heat evolved by 1 gram of the sample hour by hour, starting from the instant that quenching began. (The figures for the first hour have been corrected for the heat introduced into the calorimeter by the sample, owing to the difference between their temperatures.) The last column of the table gives the total heat, as found by extrapolation.

Table 1 gives the results secured in successive hardening-aging cycles for Sample 5 (5 cycles) and for Samples 8, 21 and 41 (4 cycles each) at 19.2°.

The figures in this table enable us to draw the following conclusions.

1. There is an appreciable difference among the various runs listed in the table, both in the amount of heat evolved per hour and in the total heat evolved. In 10 of the tests out of 17 (these tests being denoted by dots in the table), however, the results are very close. In these tests the total heat evolved was computed from averaged data.

2. It is worthy of note that the runs that give identical results all represent the last hardening-aging cycles for the given sample, i.e., the initial hardening-aging cycles yield unreproducible results, whereas the results become reproducible in the ensuing cycles.

3. The heat evolved in the initial cycles is lower in some instances (such as Samples 5 and 8) than in the subsequent cycles, while in other instances (Sample 21) the converse is true.

4. The greatest discrepancies are manifested by the results observed during the first hour of aging. This is quite understandable, inasmuch as some 40% of the total heat is evolved during the first hour.

TABLE 1

Heat Evolved During Aging After Hardening the Alloy (at 19.2°).

Sample No.	Hardening Cycles	Heat evolved by 1 gram of alloy (thousandths of a calorie) After 1st Hour	After 2nd Hour	After 3rd Hour	After 4th Hour	After 5th Hour	After 6th Hour	Total heat
5	1	140	73	33	24	18	-	340
	2·	182	76	46	40	30	-	446*
	3	216	106	70	52	36	-	568
	4·	188	82	49	40	-	-	446
	5·	195	76	52	-	-	-	446*
8	1	123	69	48	36	-	-	387
	2	135	63	51	33	27	-	387
	3·	168	78	45	33	27	-	446*
	4·	180	81	51	39	-	-	446*
21	1	213	102	72	-	-	-	574
	2	213	102	66	48	-	-	552
	3·	177	78	57	42	-	-	446*
	4·	165	75	54	39	-	-	446*
41	1	169	92	59	45	-	-	499
	2	193	71	48	30	-	-	446*
	3·	163	77	53	39	-	-	446*
	4·	190	74	50	36	27	21	446*
Mean of the runs denoted by dots		179	77	51	39	28	21	446

TABLE 2

Heat Evolved During Aging After Hardening the Alloy (at 26°).

Sample No.	Hardening Cycles	Heat evolved by 1 gram of alloy (thousandths of a calorie) After 1st Hour	After 2nd Hour	After 3rd Hour	After 4th Hour	After 5th Hour	Total heat
5	1	289	103	67	67	-	813
	2	283	109	94	64	-	862
	3	268	91	79	55	-	718
	4	234	88	73	49	-	718
	5	240	97	70	64	51	718
	6	231	97	70	61	49	718
	7	243	97	70	61	-	718

5. The decrease in the thermal effect follows a logarithmic curve in all the tests, beginning with the second hour of the process, i.e., beginning with the second hour the decomposition of the solid solution behaves like a first-order reaction. This enables us to extrapolate the experimental data. The

*Calculated from the mean of the ten runs denoted by a dot (·).

error involved in this extrapolation is insignificant, since most of the heat evolved (80-90%) has been measured experimentally.

The results secured in seven consecutive hardening-aging cycles at 26 with Sample 5 are listed in Table 2.

The following inferences may be drawn from the figures listed in this table.

1. Much more heat is evolved during aging at 26° than at 19.2°. This does not agree with Czochralski's findings [4] on duraluminum cited above. Apparently, at 26° the aging process involves much greater changes in the solid solution.

2. There is very little difference between the kinetics of the evolution of heat at 26° and at 19.2°. This also contradicts Czochralski's findings for duraluminum [4].

3. As was the case with the tests run at 19.2°, the results of the first two hardening-aging cycles at 26° differ from those secured in the subsequent cycles. On the other hand, the results of all other cycles than the first two are in good agreement.

The test in which the sample was quenched in a massive metal block exhibited a much smaller thermal effect of aging (by a factor of 8 to 10) than in the tests where the sample was quenched in water. This demonstrates the extent to which the aging process depends upon the rate of cooling of the sample during quenching. There was no use in making a study of so small a thermal effect in the calorimeter. It is quite likely that the rate at which the samples were cooled was not identical from one test to another even when they were quenched in water, this being one of the reasons for the lack of reproducibility of the experimental results.

c) Heat of aging after recovery.

In our experiments on the heat evolved during aging after recovery, we began by selecting the recovery conditions (soaking time and temperature) that would cause the sample to give off the maximum heat during aging. As we see from Table 3, these conditions (which fully agreed with Petrov's findings) were: a temperature of some 250° and a time of 15 minutes. Lower temperatures (187° in Test 2) and higher temperatures (302° in Test 1) both diminish the amount of heat evolved. Increasing the soaking time (Test 4) likewise diminishes the heat evolved, while reducing the soaking time to 6 minutes (as in Test 3) has hardly any effect.

In the next five tests (Nos. 5-9 in Table 3) the runs were made at approximately identical conditions, and their results agree fairly well. In the absence of any data, all that we could do in these cases was to estimate the total heat evolved approximately by means of extrapolation; it was found to be about 0.12 calorie per gram.

Comparison of the results of these tests, and with the figures listed in Table 1, leads to the following conclusions.

1. The heat evolved during aging is much less (by a factor of 3-4) after recovery than after hardening.

2. The evolution of heat during aging is much more quickly damped after recovery, the amount of heat evolved becoming immeasurably minute after 3-4 hours have elapsed.

3. The aging time after hardening (ranging from 1 to 5 days) has no

TABLE 3

Heat Evolved During Aging After Hardening the Alloy (at 19.2°).

Test No.	Sample No.	Temp. of Hardening	Duration of soaking, minutes	Heat evolved by 1 g alloy (thousandths of a calorie) After 2nd Hour	After 3rd Hour	After 4th Hour	After 5th Hour	Notes
1	41	302°	15	36	18	-	-	
2	41	187	15	21	0	-	-	
3	8	255	6	51	27	-	-	
4	41	248	30	39	12	-	-	
5	21	246	15	42	21	-	-	5 days after hardening
6	41	245	15	62	30	-	-	1 day after hardening
7	8	242	15	75	36	-	-	
8	8	251	15	63	27	12	6	1 day after hardening
9	5	245	15	66	30	-	-	5 days after hardening

significant effect upon the kinetics or the total quantity of heat evolved during aging after recovery (Tests 8 and 9 in Table 3).

Brinell hardness tests were made of two samples (5 and 21) to prove that recovery is actually achieved under the experimental conditions we had chosen, irrespective of the aging time. In the case of Sample 5 recovery was effected 1 day after hardening, the interval being 5 days in the case of Sample 21. The results of these tests are given in Table 4.

The results of these tests, which fully agree with the data in the literature, showed that the hardness of the samples rises for several days after quenching, actually returning to value close to that for the freshly quenched state after recovery.

TABLE 4

Brinell Hardness

	Sample 5	Sample 21
After hardening	53.5	54.0
1 day later	59.9	57.8
5 days later	-	67.1
After recovery	54.9	54.3

SUMMARY

1. The heat evolved during the natural aging of an Al-Cu alloy (5% Cu) after hardening becomes reproducible only after several (2-3) hardening-aging cycles.

2. The amount of heat evolved largely depends upon the aging temperature.

3. Beginning with the second hour after quenching, the heat evolved during aging drops off in accordance with a curve that approaches the logarithmic (first-order reaction).

4. The heat evolved by this alloy during aging after recovery is 3 to 4 times as small as after hardening.

5. A measurable amount of heat is evolved only during the initial stages of the aging process, this being true after recovery as well as after hardening, whereas the change in hardness continues for a much longer time.

We are sincerely grateful to Prof. M. M. Popov for his invaluable advice and guidance during this research.

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ANHYDROUS LITHIUM METANIOBATE

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The data in the literature on lithium metaniobate are very scanty; G. B. Bucky's handbook on crystal chemistry [1] cites the refractive index of $LiNbO_3$, while Sachariasen's paper [2] gives the values of a and α for the rhombohedral lattice. Neither of these sources indicates how anhydrous lithium metaniobate is obtained, nor are any physical constants given. That is why we undertook the present research.

1. Initial Preparations

Niobium pentoxide was prepared from tantalum-niobium residues, which contained oxides of iron, tin, titanium, silicon, and other elements, in addition to the oxides of tantalum and niobium.

In view of the fact that the initial material contained fluorides, this raw material was treated as follows. Individual 50-gram batches of this raw material were mixed with water to a pastelike consistency and then heated with 10 ml of concentrated sulfuric acid over a water bath until all the vapor of hydro-fluoric acid had been driven off. The mixture was then transferred to a beaker with distilled water, thoroughly stirred, allowed to settle, and decanted. The first wash waters were green, indicating the presence of divalent iron ions. The 'residues' were washed until all iron and sulfate ions had been removed.

It should be noted that not all the iron ions could be eliminated by this method, inasmuch as the raw materials were not pulverized finely enough. The deposit was washed with a 5% solution of ammonium carbonate to speed up the elimination of the sulfate ions.

The mixture of tantalum and niobium oxides was washed on a Buchner funnel and dried at 120°, after which it was transferred to a silver cup and fused with five times itsweight of a mixture of soda and caustic soda (90% Na_2CO_3 and 10% NaOH). After the resultant porous mass had hardened, it was transferred to a porcelain beaker with hot distilled water and heated to a boil, the traces of tin and silicon dissolving as sodium stannates and silicates. The sodium tantalates and niobates do not enter solution under these conditions, so that they can be separated from the foregoing impurities by thorough stirring and settling, followed by decantation of the supernatant solution. The sodium tantalates and niobates were dissolved in water, and the mixture of oxides was precipitated with dilute nitric acid, iron ions again appearing in the solution. The oxide mixture became a pure one after several successive decantations.

The oxides were dissolved in a calculated quantity of 40% hydrofluoric acid and the saturated solution was then treated with potassium fluoride. The solution was diluted with water until the hydrofluoric acid had a concentration of about 2% [3]. The precipitated crystals of potassium fluotantalate were filtered out, and the filtrate was evaporated until crystals of potassium hydroxofluoniobate settled out, which were recrystallized from an acid solution.

The niobium pentoxide was secured by precipitation from a solution of the potassium hydroxofluoniobate with ammonia; it was washed and suction-filtered on a Buchner funnel and then desiccated and calcined.

The lithium carbonate used as one component was chemically pure. Before use, the salt was dessicated to constant weight at 120°.

2. Methods of Analysis

The percentage of niobium pentoxide was determined by fusing the samples with ten times their weight of ammonium acid sulfate in a porcelain crucible, after which the alloy was treated with a 5% solution of ammonium carbonate. The niobium pentahydroxide was filtered out, dessicated, and calcined to constant weight in a porcelain crucible. The lithium oxide was determined quantitively as follows. The filtrate was evaporated to dryness in a quartz crucible and calcined to constant weight over a gas flame. The calcined residue was the lithium sulfate by weight as we know that Li_2SO_4 has no perceptible volatility under these conditions.

EXPERIMENTAL

1. Preparation of anhydrous lithium metaniobate. There is no indication in the literature of any method for the preparation of anhydrous lithium metaniobate. Quiter [4] asserts that the salt Li_5NbO_5 is formed when lithium carbonate is reacted with niobium pentoxide. Unfortunately his paper does not indicate the method used in analyzing this salt. We produced lithium metaniobate in two ways. In the first, we borrowed the method used by Joly [5] to prepare potassium metaniobate.

1.5 g. of lithium carbonate, 5.3 g. of niobium pentoxide, and 0.52 g. of lithium fluoride were thoroughly mixed together, and the mixture was transferred to a silver crucible. The mixture was heated in a crucible furnace equiped with a thermocouple. The roasting temperature was 700°. After the crucible had cooled, its contents were treated with water to remove the lithium fluoride. After the slight excess of lithium carbonate had been removed by decantation together with the lithium fluoride, distilled water was added. This produced an extremely stable opalescent turbidity, which disappeared completely only after 10 days had elapsed. A sample of the transparent solution cautiously taken with a tiny pipet indicated the absence of the fluorine ion in the solution. The resultant salt was analyzed.

Samples: 0.1567 and 0.1944 g.

	Found		Calculated for $LiNbO_3$
Nb_2O_5	0.1421 g. or 90.08%;	0.1749, or 89.99%	89.90%
Li_2O	0.0161 g. or 10.21%;	0.0196, or 10.24%	10.10%

In the second method equimolecular quantities of lithium carbonate and calcined niobium pentoxide were thoroughly comminuted in an agate mortar and then transferred to a silver crucible and heated for 4 hours to 700° in a crucible furnace. The end of the reaction was determined by the constancy of the crucible's weight. As in the previous case, the resultant salt was faintly yellow; microscopic examination disclosed minute crystals in the shape of stubby prisms. The salt was analyzed.

Samples: 0.1781 and 0.1693 g.

	Found		Calculated for $LiNbO_3$
Nb_2O_5	0.1599 g. or 89.78%;	0.1521 g. or 89.82%	89.90%
Li_2O	(differences) 10.12%;	(differences) 10.18%	10.10%

2. Specific gravity of anhydrous lithium metaniobate. The specific gravity was determined in a pyknometer, using toluene.

Table 1 gives the specific gravity of the anhydrous lithium metaniobate prepared by both methods.

TABLE 1

Specific Gravity of Anhydrous Lithium Metaniobate Prepared by Different Methods

No.	Method of preparing anhydrous lithium metaniobate	Specific Gravity
1	Fusing together equimolecular quantities of Li_2CO_3, LiF and Nb_2O_5	4.283
2	Fusing together equimolecular quantities of Li_2CO_3 and Nb_2O_5	4.308

The melting point of anhydrous lithium metaniobate was determined in a corundum crucible, using the freezing point. Temperature was measured with a platinum-platinum/rhodium thermocouple, which had been calibrated in the following molten salts: $K_2Cr_2O_7$, NaCl and Na_2SO_4. The melting point was measured in the crucible furnace, the melting point being found to be 1164±2°.

After the crucible had cooled, the lithium metaniobate had a clearly marked crystalline structure; the crystals were yellow.

SUMMARY

1. Anhydrous lithium metaniobate has been produced by two methods.

2. The melting point of anhydrous lithium metaniobate has been found to be 1164±2°.

3. The specific gravity of anhydrous lithium metaniobate, as determined in a pyknometer with toluene, was 4.283-4.308, depending upon the method used in producing the salt.

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HYDROXOTRIFLUOBORATES

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I. G. Ryss was the first [1] to synthesize and identify a hydroxotrifluoborate – a potassium salt;* previous reports by various authors on the preparation of substances to which such a formula might be assigned were incorrect, since the methods they employed yielded mixtures whose properties were essentially different from those of hydroxotrifluoborates. Travers and Malaprade [2] apparently secured a fairly pure KBF_3OH, but they assigned it the incorrect formula of $K_2B_2F_6 \cdot 1\frac{1}{2}H_2O$

The synthesis of KBF_3OH by the same method was described by Wamser [3] considerably later than the publication of Ryss's paper [1].

Our investigations of the kinetics of the formation of HBF_4 in mixtures of hydrofluoric and boric acids have shown that the process velocity rises considerably with the overall solution concentration and with an increase in the $\frac{HF}{H_3BO_3}$ ratio. We succeeded in interpreting the experimental data on the basis of the following process mechanism [4].

When HF and H_3BO_3 are mixed together, boron fluoride monohydrate, HBF_3OH, which behaves in solution like a strong acid, is formed nearly instantaneously. The undissociated part of the HBF_3OH, which is in equilibrium with the H^+ and BF_3OH^- ions, enters into a bimolecular reaction with the excess HF, forming HBF_4 - this process may be traced as time elapses.

The synthesis of KBF_3OH by adding H_3BO_3 to a suspension of KHF_2 chilled to 0° is based upon the following considerations: the low temperature and the low acidity of the mixture retard the conversion of the BF_3OH^- into BF_4^-. The high concentration of the K^+ in the resultant solution promotes the rapid throwing down of a KBF_3OH precipitate.

The excess F^-, formed in the reaction:

$$2KHF_2+H_3BO_3=KBF_3OH+KF+2H_2O, \qquad (1)$$

tends to lower the acidity of the solution; at the same time there is no need to fear the reaction:

$$BF_3OH^-+F^-=BF_4^-+OH^-, \qquad (2)$$

inasmuch as the combination of the equilibrium constants for the hydrolysis of BF_4^-[5], the dissociation of the water, and the dissociation of HF yields an equilibrium constant $K_2=6.1\cdot10^{-8}$. for Equation (2).

*There is a typographical error in the paper: 10 g. of H_3BO_3 is used for 25g. of KHF_2. The molar ratio $KHF_2:H_3BO_3=1.98$ is given correctly.

1. Synthesis of KBF_3OH from KHF_2, HF, and H_3BO_3

It has been shown that, notwithstanding the increased acidity of the solution, KBF_3OH may be produced by mixing together KHF_2, HF, and H_3BO_3 in the quantities specified by the following equation:

$$KHF_2+H_3BO_3+HF=KBF_3OH+2H_2O. \quad (3)$$

Example: 0.1 mol of KHF_2* was added to 4.1 g. of hot hydrofluoric acid, containing 0.1 mol of HF, weighed out in a platinum cup. After the salt had dissolved, the solution was rapidly chilled to 0° to form minute crystals, and then 0.1 mol of H_3BO_3 was added with thorough stirring. The reagents dissolved at once, a thick precipitate of KBF_3OH beginning to settle out of the transparent solution within 1 - 2 minutes. The whole mass solidified after standing on ice for half an hour. Suction-filtering and drying of the precipitate yielded 11.6 g. of the air-dry salt. The theoretical yield is 12.39 g, according to Equation (3).

Part of the salt was recrystallized in the 50-0° temperature range. The recrystallized product was dried, first at room temperature, and then in vacuum at 70°, 2.4 g. of the original salt yielding 1.97 g.

Analysis of the Salt

	Calculated		Theoretical
Consumption of alkali with $CaCl_2$ and methyl orange present	1.992; 1.987	mols / 123.93 g of salt	2.000
Per cent boron.	8.86; 8.84		8.73

This confirms the feasibility of recrystallizing the salt mentioned above, contrary to Wamser's erroneous assertion [3]. It was found that KBF_3OH does not decompose when agitated for a long time with ethyl or isoamyl alcohol, nor does it dissolve in these alcohols.

2. Synthesis and Properties of $NaBF_3OH$

Sodium bifluoride was prepared by adding a calculated quantity of a Na_2CO_3 solution to hydrofluoric acid. The precipitate was suction-filtered, washed on a paraffin-coated Buchner filter, and dried at 100°. The product contained 99.43% and 99.09% $NaHF_2$, the average being 99.26% (determined by alkali titration). The synthesis of $NaBF_3OH$ was difficult because of the high solubility of the salt, causing the BF_3OH' ion to undergo further transformations in solution. Moreover, the low solubility of the NaF interferes with a reduction of the solution acidity.

In our initial experiments we studied the feasibility of preparing $NaHF_2$ by a process similar to the one described by Equation (3):

$$NaHF_2+HF+H_3BO_3=NaBF_3OH+2H_2O. \quad (4)$$

When 51% hydrofluoric acid, $NaHF_2$, and H_3BO_3 are mixed together at 0°, the mixture does not dissolve completely. The precipitate apparently contains some $NaBF_3OH$, inasmuch as a precipitate with the following composition: B 9.21%, acidity 15.4 milliequivalents per gram of salt,** constituting contaminated $NaBF_3OH$, was recovered after filtration of the slighly heated mixture, followed by recooling of the filtrate. In the subsequent tests, the filtrate separated without heating

*The potassium bifluoride, produced in the usual manner, was 99.97% pure.

** Determined in the presence of $CaCl_2$ and methyl orange.

was quickly evaporated in vacuum at room temperature, but the resultant salt samples were even more contaminated.

Purer samples were prepared by a process resembling the one described by Equation (1). Either H_3BO_3 was added to a mixture of $NaHI_2$ and water chilled to 0° or $NaHF_2$ was added to a mixture of H_3BO_3 and water. The molar ratio of $NaHF_2$:H_3BO_3 equaled 2. 50 to 100 ml of water was added to 1 mol of boric acid. After the reagents had been stirred together for half an hour, the small quantity of a NaF precipitate was suction-filtered out, the filtrate being either evaporated in vacuum or salted out by adding four times the volume of alcohol. The differences in the composition of the salt as prepared by the different variants employed were not significant, though the purer samples were secured when salting out was used. The mean yields of the salt approached 50% of the theoretical (when 0.05 mol of H_3BO_3 was used).

The composition of some of our samples (Nos. 1-6) was as follows:

	1	2	3	4	5	6	Theoretical
Acidity, milliequivalents per gram of salt	17.82	17.40	17.50	17.20	17.62	17.01	18.55
Per cent boron*	9.98	9.92	9.95	9.92	9.75	9.85	10.03

$NaBF_3OH$ is very highly soluble in water, but is not very hygroscopic (the foregoing analyses refer to the air-dry state). The salt is not decomposed when treated with ethyl alcohol, being very slightly soluble in it (about 0.3%). Its chemical properties resemble those of the KBF_3OH described previously [1] and differ considerably from the properties of the substance prepared by Meerwein and Pannwitz, which they erroneously described as $NaOH \cdot BF_3$ [5].

3. Decomposing KBF_3OH Solutions

In our first report on the synthesis and properties of KBF_3OH [1] we noted that the titratable acidity of solutions of this substance diminishes with time, because of the partial conversion of the BF_3OH' into BF_4'. Both the acidity that can be titrated in the presence of $CaCl_2$ and methyl orange (the alkali consumption is two equivalents per gram ion of BF_3OH [1]) and the percentage of boric acid measurable after the first titration is completed and after invert sugar and phenolphthalein have been added (1 equivalent of alkali per gram ion of BF_3OH [1]) drop off. The decomposition of the BF_3OH' follows either of these two possible patterns:

$$3BF_3OH' \rightleftarrows 2BF_4' + H_3BO_3 + F' \qquad (5)$$

or

$$2BF_3OH' \rightleftarrows BF_2(OH)_2' + BF_4' . \qquad (6)$$

Both of these equilibria are possible.

Inasmuch as BF_3OH' is titrated quantitatively by using two mols of NaOH per gram ion of BF_3OH', it may be said that even if $BF_2(OH)_2$ is formed in the aqueous solution, it is likewise titrated at the rate of 1 mol of NaOH per gram ion.

It is therefore impossible to compute the degree of decomposition of the BF_3OH' from the decrease in the titratable acidity. We can, however, calculate

*As before, the boron in the BF_4' was not determined.

**Samples 1-3 were prepared by salting out with alcohol; samples 4-6 by evaporation.

the number of mols of BF_4' formed from 1 mol of the BF_3OH' initially present (this ratio is denoted below by $\underline{x}$).

Denoting the calculated consumption of alkali in the first and second titrations of the undecomposed solution by $\underline{v_1}$ and $\underline{v_2}$, and the consumption of alkali in titrating the same quantity of the partially decomposed solution of KBF_3OH by v_1' and v_2', we can easily derive two expressions for $\underline{x}$ from the stoichiometrical proportions:

$$x = \frac{2n}{3}\left(1 - \frac{v'_1}{v_1}\right), \qquad (7)$$

$$x = 1 - \frac{v'_2}{v_2}. \qquad (8)^*$$

According to Equations (5) and (6), the maximum values that $\underline{x}$ can have are 0.667 and 0.500. The decomposition of the KBF_3OH solutions with time was followed experimentally at the temperatures of 30.0, 70.0, and 90.2°, which were maintained to within ±0.05° in an automatically regulated water thermostat.**

Solutions of three different concentrations were tested at each of the foregoing temperatures.

A weighed amount of water was kept in a flask*** within the thermostat until its temperature leveled off. Then a weighed amount of KBF_3OH,**** was placed in the flask and quickly dissolved by agitating the latter.

Samples taken with a pipet at equal intervals of time were emptied into a flask packed in snow (to "chill" the mixture), after which the sample was analyzed by double titration with 0.1N alkali solution. The normality of the alkali, prepared from metallic sodium, was determined against potassium biphthalate and bi-iodate, and against borax for the second titration.

The average weight of the samples taken was determined by weighing several samples specially taken for this purpose. Samples having a molality of 0.8-1, 0.33, and 0.11 weighed approximately 2, 5, and 10 grams, respectively. The results of our measurements are reproduced in Figs. 1 - 4. The values of $\underline{x}$ as calculated from the first titration (determination of "acid fluorine") are denoted by $\underline{x_F}$; those calculated from the boric-acid titration are denoted by x_B.

The agreement between the values of x_F and x_B may be regarded as satisfactory, if we remember that any error in the first titration produces an opposite error in the results of the second titration. The fluctuations in the values of x_F and x_B are also caused by departures in the weights of the individual samples from the mean weight. This factor was even greater in the highly concentrated solutions.

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*In view of the fact that the salt sample used contained minute quantities of excess boric acid, a suitable small correction has been applied in the computations.

**In the series of tests run at 30° the temperature sometimes dropped to 23-24° during the night owing to power failure.

***Paraffin-coated flasks were used in the 30° tests, and rubber flasks in the tests run at 70.0 and 90.2°.

****The salt sample used in this part of the experiment contained 98.3% KBF_3OH and 2.46% boric acid (partly dehydrated).

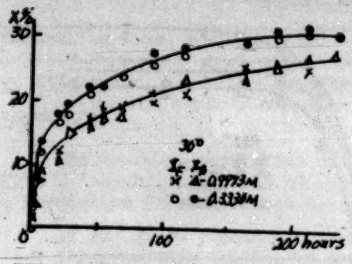

Fig.1.

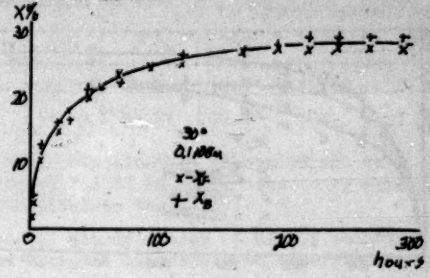

Fig.2.

At 90°, the yield of BF_4' attains equilibrium within the course of 1½ -2 hours, the state of equilibrium being reached within 5 to 6½ hours at 70°. Owing to the high temperature coefficient of the reaction rate, the state of equilibrium was reached after 240 hours at 30°, but only in dilute solutions.

As the solution is diluted, the equilibrium yield of BF_4' rises slightly, the effect of dilution being more pronounced in the 0.33 - 0.11 molality range.*

In this concentration range the process described by Equation (5), involving an increase in the number of dissolved particles, apparently acquires greater importance.

A rise in temperature produces a slight increase in the equilibrium yield of BF_4', which is more perceptible in a more diluted solution. This indicates that the formation of BF_4' is a very slightly endothermic process.

The heat of reaction [s] may be calculated by summation of the heats of the partial reactions:

$$2BF_3OH' + 2HF_{aq} = 2BF_4' + 2H_2O + 6.46 \text{ kcal.} \quad [8]$$

$$H^+ + BF_3OH' + 2H_2O = H_3BO_{3aq} + 3HF_{aq} - 13.74 \text{ kcal.} \quad [7]$$

$$HF_{aq} = H^+ + F' + 3.05 \text{ kcal.} \quad [8]$$

$$3BF_3OH' + 2BF_4' = H_3BO_{3aq} + F' - 4.2 \text{ kcal.}$$

In the reaction involved in the dissolution of boric acid in hydrofluoric acid, about 4.6 kcal. are evolved per mol of HF, i.e., somewhat more than when HF reacts with the BF_3OH'. If the hydroxyl groups in the boric acid are replaced by fluorine gradually, it is probable that each successive substitution stage involves the liberation of less heat, and the heat of the reaction $BF_2(OH)'_2 + HF_{aq} = BF_3OH' + H_2O$ must be less than 4.6 kcal. Then the heat absorbed in Reaction (6) must be less than 4.6 - 3.2 = 1.4 kcal, so that this equilibrium must be even less dependent upon temperature than was the case for the equilibrium (5).

When we compare the curves of $\underline{x} = \underline{f}$ (time) for the various solution concentrations, we find that the formation of BF_4' in KBF_3OH solutions is a process the order of which is somewhat less than unity. Endeavors to have the shape of each of the curves represent an equation of a reversible first-order process for each course taken by the reactions** were unsuccessful - as $\underline{x}$ increased, the formation of BF_4' decreased faster than the above hypothesis presupposed. The reaction is apparently highly complex, the direct reaction

* See Footnote next page. ** See footnote next page.

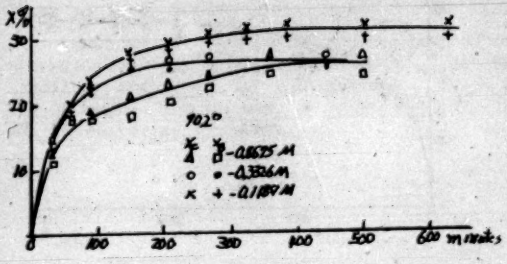

Fig.3.

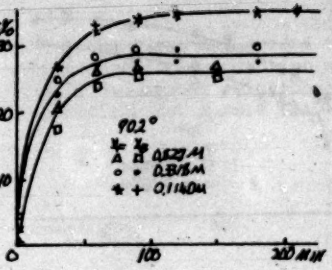

Fig.4.

being slowed down by its own products (the increase in pH, due to an accumulation of fluorine ions in the solution, may play a part).

4. The Solubility of KBF_3OH

The sample of salt used in this section of our investigation contained 8.82% B. The consumption of alkali in $CaCl_2$ and methyl orange was 1.970 mol per 123.93 g. of the salt.

5.5 g. of KBF_3OH was mixed with 30 ml of water in a paraffin-coated test tube, immersed in a Dewar flask filled with ice. The paraffin-coated stirrer was driven at 60 rpm by a Warren fractional hp. motor. Samples of the solution were taken at regular intervals, and separated from the precipitate at 0°. The results of our analysis of these samples are given in Table 1.

TABLE 1

Saturation of Water With KBF_3OH at 0°.

Saturation time, hours	0	2	19	43	67	91
y_1 ml/gram (0.0947 N NaOH) . .	8.83	10.87	10.87	10.88	10.86	10.84
y_2 ml/gram (0.0933 N NaOH) . .	4.77	5.92	6.03	6.03	6.06	6.05

The maximum consumption of alkali (at 43 hours) is equivalent to a KBF_3OH "solubility" of 6.4% (according to y_1) or 6.55% (according to y_2).***

The results of our solubility measurements at 45.1° are given in Table 2. Here the test tube was immersed in a thermostat, the temperature of which was kept constant within ± 0.03°. 10 g. of water was used for 10 g. of the salt.

*The figures for the solution of 0.3330 molality at 30° do not tally with the behavior patterns outlined above. It may be that an error crept into this series (solution concentration), causing a systematic exaggeration of several per cent in the computed values of x

**As has been shown previously [8], the decomposition of BF_4' in an aqueous solution is described by an equation for a first-order reaction.

***Applying a correction for the excess boric acid in the salt and assuming that all of it is dissolved.

TABLE 2

Saturation of Water With KBF_3OH at 45.1°

Saturation time, minutes	30	70	140	205	265	325	385
v_1 ml/gram	53.77	55.53	53.78	60.22	56.73	57.09	57.38
v_2 ml/gram	29.1	30.56	32.62	34.25	32.16	32.13	31.99

The maximum consumption of alkali (after 205 minutes) is equivalent to a KBF_3OH "solubility" of 35.3% (according to v_1) or 37.1% (according to v_2 applying a correction for the excess boric acid contained in the salt).

It should be emphasized that the gradual decomposition of KBF_3OH solutions (see the preceding section of this paper) makes it impossible to determine the true solubility of the salt. The formation of KBF_4 must lower the solubility of the KBF_3OH slightly. The accumulation of the freely soluble $KBF_2(OH)_2$ must reduce the solubility of the KBF_3OH considerably, but since the former salt is likewise titrated by the alkali, the measured solubility of KBF_3OH is too high. Lastly, the accumulation of boric acid must tend to overstate the "solubility" of the KBF_3OH as computed from v_2.

Still, the calculated values of the "solubility": 6.4% at 0°, 11% at 14° [1], and 35.3% at 45.1° are evidence that the hydroxotrifluoborate is much more soluble than potassium tetrafluoborate.

SUMMARY

1. A new method of synthesizing potassium hydroxotrifluoborate, by reacting a mixture of potassium bifluoride and hydrofluoric acid with boric acid, is described.

2. The synthesis of sodium hydroxotrifluoborate is described. This salt is very freely soluble in water. Its other chemical properties resemble those of the potassium salt.

3. The tetrafluoborate is formed in solutions of the hydroxotrifluoborate, a state of equilibrium between the two being reached that depends but little upon the temperature or the concentration of the solution.

4. The rate at which BF_4' is formed drops slightly as the initial concentration of BF_3OH' is increased and rises sharply with rising temperature.

5. The solubility of KBF_3OH is 6.4% and 35.3% at 0° and 45.1°, respectively.

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*See C.B. English translation, page a-281.
**See C.B. English translation, page a-291.

I. A. KABLUKOV'S AND D. P. KONOVALOV'S RESEARCHES ON THE ELECTROCHEMISTRY OF NONAQUEOUS SOLUTIONS

D. A. Pospekhov

The present article sets forth several comments on the significance of the researches of I. A. Kablukov [2,3] and of D. P. Konovalov [5-8] on electrically conducting nonaqueous solutions. Notwithstanding the rather wide knowledge of these researches, insufficient light has been shed upon their importance. We shall endeavor to do so in connection with the Nernst-Thomson rule.

As we know, that rule was set forth almost simultaneously by Thomson [28] and Nernst [24,25]. The substance of the rule is that the attractive force between the ions of the dissolved substance varies inversely with the dielectric constant of the solvent. This gave rise to the concept of the dissociating power of a solvent. Nernst indicated the parallelism between the dielectric constant and the conductance of a solution. Subsequently, Walden [30,31] derived the expression $\varepsilon_1 \sqrt[5]{v_1} = \varepsilon_2 \sqrt[5]{v_2} = \text{const.}$ (ε = dielectric constant, and v = dilution), for tetraethylammonium iodide in a large number of solvents, the expression being valid for equal degrees of dissociation.

The Nernst-Thomson rule and the cited researches of Walden were criticized by various authors, principally V. A. Plotnikov [10-14] and M. I. Usanovich [18-20]. Plotnikov [13] asserted that Walden's expression was highly approximate for a large number of cases: in the given solvent pair $N(C_2H_5)_4I$ may have identical degrees of dissociation at equal dilutions, but the ratio of the values of ε does not equal unity for these solvents, lying rather between 1.2 and 1.5; the same salt may exhibit degrees of dissociation that differ by a factor of 1.5 in two solutions with approximately equal values of ε at equal dilutions.

In stating his rule, Thomson cited no concrete examples, while Nernst illustrated the rule with a table on p. 49.

In support of the rule, Nernst cited the results previously obtained by Kablukov [3] in his researches on solutions of hydrogen chloride in various organic solvents, noting the parallelism between conductance and dielectric constant, the conductance being extremely low in benzene, xylene, and hexane (ε = 2.2 - 2.4), appreciably higher in ether (ε = 4.4), and much higher in various alcohols, being highest in methanol (ε = 33.7) and dropping progressively in ethyl, propyl, and isobutyl alcohols, the ε being 25, 22, and 19, respectively. At the time the ε of isoamyl alcohol was unknown, so that Nernst made no mention of Kablukov's findings on the solution of HCl in that substance. The ε of isoamyl alcohol is 15,

Medium	Dielectric Constant	Electrolytic dissociation
Gas space	1.0	Not measurable at ordinary temperatures
Benzene	2.3	Extremely small, but definitely established conductivity, indicating traces of dissociation
Ethyl alcohol	25	Clearly perceptible
Water	80	Very strong

i.e., the lowest in this series, which agrees with the minimum conductance of HCl observed by Kablukov. In addition to Kablukov's researches, Nernst also mentions the later paper by Wakeman [29] who reported that the dissociation of acids dissolved in water decreased as alcohol was added, adding that this fact was a result of the decrease in the ε of the medium. As we see, Kablukov's findings were, at bottom, the main foundation for the rule in question. No mention has been made of this up to the present time. Plotnikov, for example, cites [13] some excerpts from Nernst's paper [25] without saying a word about Kablukov's findings in this connection. In his discussion of the Nernst-Thomson rule, Usanovich [18-20] likewise fails to indicate the significance of Kablukov's researches in this connection. In Walden's comprehensive work on the electrochemistry of nonaqueous solutions [30], the author often refers to this research of Kablukov's on various occasions, but does not mention the part played by the latter in the establishment of the rule.

Plotnikov found various instances of rather high conductance in solvents with very low dielectric constants [10-13] [solutions in bromine ($\varepsilon = 3.18$), benzene ($\varepsilon = 2.3$), ether ($\varepsilon = 4.4$), and chloroform ($\varepsilon = 5.0$)]. This was of fundamental importance in establishing the limits within which the Nernst-Thomson rule was applicable. Some authors (Plotnikov, Usanovich, and Fredenhagen) reject this rule entirely because of these and similar facts [10-14, 18-20, 22, 27].

With the passage of time, Walden's opinions of the role of the dielectric constant in conducting solutions changed considerably, influenced by the researches of the authors cited [10-14, 18-20, 22, 27] as well as by his own experiments [32,33] that postdated his initial researches [30,31]. His lecture at the Mendeleev Jubilee Congress in 1934 [1], where he acknowledged the ability of media with extremely small values of ε to dissociate dissolved substances into ions completely, is highly characteristic in this connection. Plotnikov made special mention of this point [14], asserting that "..... when Walden began his research, he spoke of nothing but the dissociating power; but now he has reached the conclusion that many substances become electrolytes when interacted with suitable solvents. I have always regarded electrochemical conformity as the most important factor in conductance phenomena."

Nernst, in his repeatedly republished Theoretical Chemistry, comments on the Nernst-Thomson rule without saying a word about the fact of appreciable conductance in media with low values of ε.

We shall show that the facts set forth in the papers by D. P. Konovalov, which were published in 1892-1893 [5-8], should have been taken into account in the period that immediately followed the establishment of the Nernst-Thomson rule (1893). Konovalov investigated the conductance of binary systems consisting of aromatic amines and aliphatic acids, finding appreciable conductance existing in systems consisting of aniline as one component and acetic, propionic, or butyric acid as the other [5,8]. It should be noted that the dielectric

constants of these acids were unknown in 1893 [18], so that Nernst, in his commentaries on the rule he had propounded [24,25], made the (incorrect) assumption that these constants must lie between the values of the respective constants for the alcohols and water. Thus the absence of any mention of Konovalov's researches in the cited paper by Nernst was quite natural. The dielectric constants of acetic, propionic, and butyric acids were reported by Jahn and Moller [23] in 1894 (in a paper published in the same issue of the journal as that of Nernst [25]) to be 6.4 (at 20°), 3.14 (at 19°), and 2.9 (at 16°), respectively.

This made appropriate comment on the Nernst-Thomson inescapably necessary, inasmuch as the facts established by Konovalov were evidence of the existence of appreciable conductance in solutions possessing low dielectric constants, contrary to the rule. Although the literature on the rule eventually became rather extensive, no light has been shed on the significance of Konovalov's researches for the rule down to the present time. Plotnikov [13], in a special discussion of Konovalov's views regarding the cause of the conductance of solutions, makes no mention of the latter's researches dealing with the Nernst-Thomson rule. In Waldens's monograph on the electrochemistry of nonaqueous solutions [30], he refers repeatedly to Konovalov's researches, but not in connection with this rule.

Konovalov's investigations [5-8] have been checked experimentally and discussed repeatedly from various standpoints [4,9,13,17,21,26]. The conductance of the aniline-acetic acid system has recently been measured by Cherbov [21], Trifonov and Cherbov [17], Klochko and Chanukvadze [4], and Naumova [9], their findings being close to those secured by Konovalov. There is, therefore, no ground for doubting Konovalov's findings on the binary systems consisting of aniline and propionic or butyric acid. Let us say at once that the conductance of systems containing aniline decreases in the following order: acetic acid – propionic acid – butyric acid, i.e., parallel to the decrease in their dielectric constants. We reproduce some of Konovalov's data for a temperature of 21°, the aniline concentration being always given in per cent by weight (first figure) and in molar per cent (second figure) [5,8].

Aniline – acetic acid system: 4.00 (2.62)% $\underline{x} = 0.267 \cdot 10^{-4}$; 20.60 (14.95)% $\underline{x} = 2.705 \cdot 10^{-3}$; 35.01 (26.06)% $\underline{x} = 2.47 \cdot 10^{-3}$.

Aniline – propionic acid system: 14.32 (11.74)% $\underline{x} = 0.66 \cdot 10^{-4}$; 22.30 (18.59)% $\underline{x} = 0.36 \cdot 10^{-3}$.

Aniline – butyric acid system: 15.65 (14.95)% $\underline{x} = 0.6 \cdot 10^{-5}$; 27.10 (26.02)% $\underline{x} = 0.7 \cdot 10^{-4}$.

The minimum concentrations cited above for the systems containing propionic and butyric acids agree with the figures given by Konovalov.

The first paper by Plotnikov, whose findings he opposed to the Nernst-Thomson rule, goes back to 1902 [10,15] (solutions of $AlBr_3$ in C_2H_5Br). At 15 mol.% of $AlBr_3$ $\underline{x} = 0.85 \cdot 10^{-3}$, at 24.7 mol.% $\underline{x} = 2.09 \cdot 10^{-3}$. This paper was described by Patten [27] as a striking demonstration of the error of the Nernst-Thomson rule, since the ε of ethyl bromide is 8.9.

The Konovalov figures cited above indicate that they can be used even more successfully than the figures cited by Plotnikov in opposition to the Nernst-Thomson rule, since they were published at a much earlier date and refer to solvents with lower dielectric constants.

The fact that the concentration of aniline in the systems containing propionic and butyric acids is relatively high in no way diminishes the

merits of Konovalov's figures as evidence against the Nernst-Thomson rule, since the dielectric constant of aniline is low (7.12 at 16°), as Jahn and Moller established in the same paper in which they gave the values of ε for the acids mentioned above [23].

Subsequently Plotnikov found a number of other instances of high conductance in solvents possessing low dielectric constants. In most of these cases the values observed by Plotnikov were of the same order of magnitude as in the papers by Konovalov. For example, when the percentage of phospheric acid in ether ranged from 12.7 to 54.1% by weight, it had a $\underline{x}$ ranging from $0.736 \cdot 10^{-5}$ to $0.838 \cdot 10^{-3}$ [12]. Concentrations of $SbBr_3$ in bromine, ranging from 7.1 to 47.7% by weight, had values of $\underline{x}$ ranging from $0.14 \cdot 10^{-6}$ - $98 \cdot 10^{-6}$. Solutions of the coordination compound of dimethylpyrone with trichloroacetic acid, $C_7H_8O_2 \cdot 2CCl_3COOH$, in benzene, chloroform, and ethyl bromide exhibited conductance ranging from 10^{-4} to 10^{-3} (in C_2H_5Br $\varepsilon = 8.9$, i.e., the largest value in this series even to 10^{-2}) [11,13]. PBr_5 in bromine exhibited a value of α ranging from $0.87 \cdot 10^{-8}$ at 3.31% by weight to $5.34 \cdot 10^{-2}$ at 36.0% by weight [15]. These and similar findings enabled Plotnikov to take a stand in 1908 [13] against the Nernst-Thomson rule as not being in agreement with actuality.

To sum up, it may be asserted that the part played by I. A. Kablukov and D. P. Konovalov in the evolution of one of the major hypotheses of the electrochemistry of solutions has been considerably minimized.

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THE PHYSICO-CHEMICAL ANALYSIS OF THE BINARY SYSTEMS OF UREA AND THE PHENOLS

I. CONDUCTANCE, VISCOSITY, AND DENSITY

D. E. Dionisyev and N. Z. Rūdenko

Research on the following systems: urea – pyrocatechol, urea – resorcinol, and urea – hydroquinone by the thermal method of physico-chemical analysis has shown [1] that urea enters into a 1:1 compound with these diatomic phenols.

As we know, the presence of chemical interaction is often manifested on the curves of other system properties, this being particularly true of rational systems. In irrational systems the compounds that form are partially dissociated at the melting point, while in the liquid phase they may be dissociated completely and not exhibit chemical action on the curves of other properties. Although the thermal method must be regarded as the principal method of physico-chemical analysis, it must be supplemented by other methods [2]. Only a comparison of the different properties of a system, investigated at different temperatures, can furnish a reliable answer concerning the composition and stability of a chemical compound. With these considerations in mind, we made an investigation of the density, viscosity, and conductance of the binary systems cited above, besides investigating the density, viscosity, and conductance of the urea – phenol system.

Conductance was measured by the Kohlrausch method in a closed vessel with smooth platinum electrodes. An audio-frequency vacuum-tube oscillator connected to a booster was used as a source of current. To increase the precision of measurement the current minimum was fed into a two-stage vacuum-tube amplifier, from which it was fed into the indicator (high-impedance headphones and a "magic eye").

Internal friction was measured in a viscosimeter of the closed type.

We measured the density of the system mainly in order to compute the internal friction, for in most cases viscosity by itself can hardly furnish an indication of the nature of the interaction between the system's components [3]. Density was measured with a Regnault pyknometer. The temperature fluctuations in the oil thermostat employed did not exceed 0.15°.

The Urea – Phenol System

The fusibility of the urea – phenol system has been investigated by Kreman [4] and by Philip [5]. They found a compound with the composition of $CO(NH_2)_2 \cdot 2C_6H_5OH$ and a m.p. of 60.6°. The compound was highly dissociated; one of its eutectics had the same melting point as the compound itself (60.6°, its composition being 33.4 molar per cent of urea). We checked this section of the fusibility curve and confirmed these findings.

In our research we used phenol with a b.p. of 181° and a m.p. of 41°., the m.p. of the urea was 133°.

Viscosity

The viscosity was measured at 120 and 135°. The results of our measurements are listed in Table 1, the viscosity being represented in Fig. 1 as a function of the concentration, expressed in molar per cent.

As we see in Fig. 1, the viscosity isotherms are curves that are slightly concave upward.

TABLE 1

No.	Mol. % $CO(NH_2)_2$	Viscosity $\eta \cdot 10^3$ 120°	135°	No.	Mol. % $CO(NH_2)_2$	Viscosity $\eta \cdot 10^3$ 120°	135°
1	90.00	-	23.6	7	45.00	17.8	13.9
2	80.00	26.3	21.0	8	40.00	16.6	13.0
3	70.00	23.9	19.1	9	35.00	15.6	12.3
4	60.00	21.6	17.1	10	30.00	14.2	11.2
5	55.00	20.5	16.1	11	20.00	11.9	9.6
6	50.00	19.0	15.0	12	10.00	10.2	8.2

Isotherms of this sort are evidence of the absence of any chemical interaction between the system components. Nor does the calculated absolute temperature coefficient of viscosity in the 120-135° range (Table 2 and Fig.2) give any indication of chemical interaction in the system.

TABLE 2

No.	Mol. % $CO(NH_2)_2$	α_η (135-120°)
1	80.00	35.4
2	70.00	32.0
3	60.00	30.0
4	55.00	29.3
5	50.00	26.7
6	45.00	26.0
7	40.00	24.0
8	35.00	22.0
9	30.00	20.0
10	20.00	15.3

TABLE 3

No.	Mol. % $CO(NH_2)_2$	Density 120°	135°
1	90.00	-	1.1947
2	80.00	1.1751	1.1653
3	70.00	1.1360	1.1254
4	60.00	1.1148	1.1051
5	50.00	1.0776	1.0680
6	40.00	1.0522	1.0412
7	30.00	1.0350	1.0247
8	20.00	1.0103	1.0050
9	10.00	0.9974	0.9898

The density was measured at the same temperatures (Table 3). The curves showing the density as a function of the concentration are slightly concave upward, (Fig. 3).

Conductance

The conductance was likewise measured at 120 and 135°. The measurement results are tabulated in Table 4, the curves of conductance as a function of composition being reproduced in Fig. 4. In this system the conductance drops from that of phenol to that of urea along a curve that is concave upward. M. I. Usanovich [6] was the first one to observe conductance isotherms of this shape for systems in which the components did not interact chemically. It was later found, however, that conductance isotherms of this sort are encountered in systems in which chemical interaction does occur [7], as exhibited in the curve of the 'derived' conductance $x\eta$ and the curve of the conductance temperature

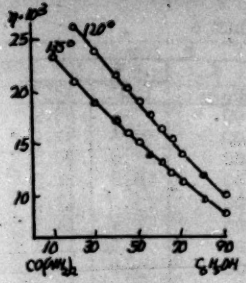

Fig.1

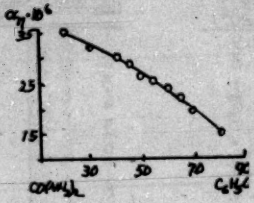

Fig.2

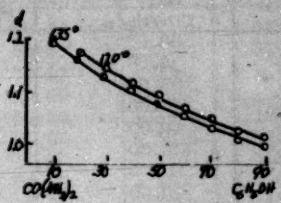

Fig.3

coefficient $\alpha_{\underline{x}}$.

We calculated the temperature coefficient of conductance within the 135-120° temperature range. The results of the calculation are given in Table 5, while the functions of concentration are plotted in Fig.5. We also corrected the conductance for viscosity (Table 6 and Fig.6). Both the temperature coefficient curve and that of the corrected conductance are smooth, without any singular points (maxima, minima, or points of inflection).

TABLE 4

No.	Mol. % $CO(NH_2)_2$	Conductance $\underline{x} \cdot 10^5$		No.	Mol. % $CO(NH_2)_2$	Conductance $\underline{x} \cdot 10^5$	
		120°	135°			120°	135°
1	90.00	-	22.8	7	45.00	4.5	8.0
2	80.00	14.2	19.5	8	40.00	3.5	6.2
3	70.00	11.4	16.1	9	35.00	2.8	5.1
4	60.00	8.7	12.8	10	30.00	2.4	4.14
5	55.00	7.3	11.0	11	20.00	0.5	2.2
6	50.00	6.0	9.7				

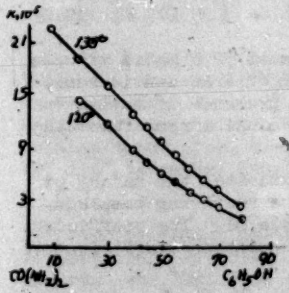

Fig.4

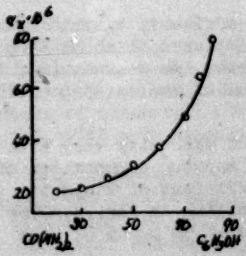

Fig.5

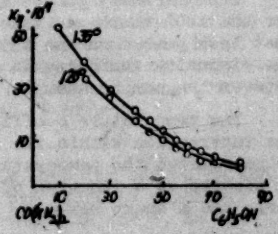

Fig.6

TABLE 5

No.	Mol. % $CO(NH_2)_2$	$\alpha_x \cdot 10^8$ (135-120°)
1	80.00	20.9
2	70.00	22.8
3	60.00	25.3
4	50.00	31.8
5	40.00	37.7
6	30.00	50.0
7	25.00	66.0
8	20.00	82.0

TABLE 6

No.	Mol. % $CO(NH_2)_2$	$\eta \cdot 10^7$	
		120°	135°
1	90.00	-	53.9
2	80.00	37.4	41.0
3	70.00	27.2	30.8
4	60.00	18.8	21.9
5	55.00	15.0	17.7
6	50.00	11.4	14.5
7	45.00	8.38	11.1
8	40.00	5.8	8.11
9	35.00	4.36	6.28
10	30.00	3.4	4.56
11	20.00	1.14	2.11

The Urea - Pyrocatechol System

A thermal investigation of the system disclosed the existence of a compound, $CO(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$ with a m.p. of 91° [1].

Pyrocatechol with a m.p. of 105° was used in this research.

The viscosity was measured at 120 and 135°, the results being listed in Table 7 and the curves of viscosity as a function of concentration being plotted in Fig.7.

TABLE 7

No.	Mol.% $CO(NH_2)_2$	Viscosity $\cdot 10^3$		No.	Mol.% $CO(NH_2)_2$	Viscosity $\cdot 10^3$	
		120°	135°			120°	135°
1	90.00	-	27.6	8	50.00	38.4	29.8
2	80.00	36.1	28.4	9	47.50	37.9	29.4
3	70.00	37.2	29.3	10	45.00	37.3	28.8
4	60.00	38.2	30.0	11	40.00	35.9	27.8
5	57.50	38.4	30.1	12	30.00	31.6	24.4
6	55.00	38.5	30.2	13	20.00	27.8	21.0
7	52.50	38.6	30.0	14	10.00	25.0	19.2

The viscosity curves exhibit a clearly visible maximum at 52.5 mol.% of urea for the 120° isotherm, which is displaced to about 55 mol.% of urea and is somewhat less peaked on the 135° isotherm. As we know [2], the presence of maxima on the viscosity isotherms is evidence of the existence of chemical interaction between the components.

The temperature coefficient of viscosity very often indicates the nature of the interaction within the system and the composition of the resulting compound. We calculated the temperature coefficient of viscosity (Table 8). The coefficient is plotted as a function of composition in Fig. 8. The temperature coefficient curve has a sharp maximum, located at 50 mol.% of urea.

The density isotherms for 120 and 135° (Table 9 and Fig.9) are straight lines. This form of density isotherms is evidence of the existence of chemical interaction rather than of its absence.

TABLE 8

No.	Mol. % $CO(NH_2)_2$	$\alpha_x \cdot 10^6$ (135-120°)
1	80.00	51.5
2	70.00	52.7
3	60.00	54.6
4	55.00	55.3
5	50.00	58.7
6	45.00	56.5
7	40.00	55.2
8	30.00	48.0
9	20.00	45.3

TABLE 9

No.	Mol. % $CO(NH_2)_2$	Density 120°	Density 135°
1	90.00	-	1.2210
2	80.00	1.2267	1.2128
3	70.00	1.2160	1.2090
4	60.00	1.2080	1.1928
5	50.00	1.1971	1.1840
6	40.00	1.1878	1.1740
7	30.00	1.1785	1.1684
8	20.00	1.1690	1.1561
9	10.00	1.1594	1.1482

Conductance

The conductance was measured at the same temperatures as were used for the viscosity. The measurements are listed in Table 10, the conductance being plotted as a function of concentration in Fig.10. As we see in Fig.10, the conductance isotherm for 120° has a minimum at about 52 mol.% of urea, while one of the isotherm's branches has a maximum at 35 mol. % of urea. As the temperature is raised, the minimum persists, being shifted toward the component with higher conductance, while the maximum vanishes. The shape of the conductance isotherms is evidence of chemical interaction. Assuming that the conductance of this system is greatly affected by the viscosity and wishing to follow the conductance curve without the action of viscosity, we eliminated the latter factor.

TABLE 10

No.	Mol. % $CO(NH_2)_2$	Conductance x $\cdot 10^5$ 120°	Conductance x $\cdot 10^5$ 135°	No.	Mol. % $CO(NH_2)_2$	Conductance x $\cdot 10^5$ 120°	Conductance x $\cdot 10^5$ 135°
1	90.00	-	26.0	8	50.00	14.5	22.3
2	80.00	16.6	25.4	9	47.50	14.6	22.0
3	70.00	15.8	24.1	10	45.00	15.0	21.8
4	60.00	15.1	22.6	11	40.00	15.4	21.6
5	57.50	14.4	22.4	12	30.00	15.6	20.5
6	55.00	14.6	22.2	13	20.00	14.0	18.8
7	52.50	14.4	22.3	14	10.00	11.8	16.3

The results of our calculation of the corrected conductance are given in Table 11, the curves being plotted in Fig.11. The maximum has vanished on the curves of the "derived" conductance, a point of inflection appearing in the region of the minimum, at 50 mol. % of urea. The curve (Fig.12) of the calculated temperature coefficient of conductance for the temperature range of 135-120° is rather complicated, with a maximum at 50 mol. % of urea.

Evaluation of Results

The viscosity isotherms of the urea - phenol system, and the curves of the temperature coefficient of viscosity, are quite smooth and slightly concave upward; the isotherms of conductance and density have the same shape, as do the curves of the "corrected" conductance and of the temperature coefficient of conductance. The curves of these properties thus do not reflect any chemical interaction within the system, and do not bear out the existence of the compounds

$$CO(NH_2)_2 \cdot 2C_6H_5OH,$$

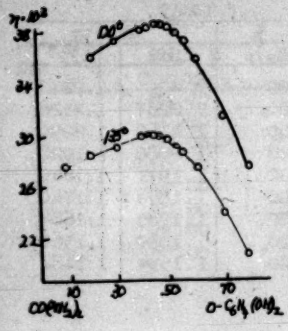

Fig.7.

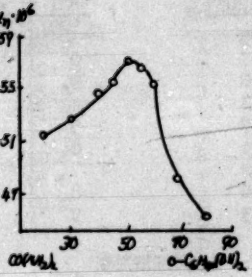

Fig.8.

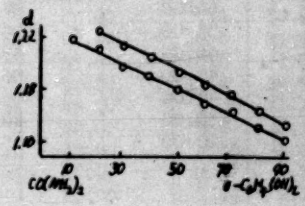

Fig.9.

TABLE 11

No.	Mol. % $CO(NH_2)_2$	$x\eta \cdot 10^7$ 120°	$x\eta \cdot 10^7$ 135°
1	80.00	60.0	72.0
2	70.00	58.9	70.5
3	60.00	57.5	68.0
4	55.00	56.3	66.9
5	52.50	55.3	66.9
6	50.00	55.5	66.5
7	45.00	55.5	63.5
8	40.00	55.1	60.0
9	30.00	49.3	50.0
10	20.00	39.0	39.5

TABLE 12

No.	Mol. % $CO(NH_2)_2$	$\frac{\alpha x \cdot 10^6}{(135-120°)}$
1	80.00	28.0
2	70.00	27.8
3	60.00	26.6
4	50.00	28.3
5	40.00	22.3
6	30.00	18.1
7	20.00	19.5
8	10.00	23.5

indicated by the fusibility method. It may be that this compound, which is dissociated rather appreciably even at its melting point, dissociates completely in the liquid phase.

In the urea – pyrocatechol system, the viscosity isotherms exhibit an irrational maximum that is shifted toward the more highly viscous urea. The conductance isotherms have a minimum at 50 mol. % of urea, while those of the "corrected" conductance exhibit a point of inflection in this region. The curves of the temperature coefficients of viscosity and of conductance have maxima located exactly at 50 mol. % of urea.

The shapes of the curves of these properties are indisputable evidence of chemical interaction within the system. The maximum and the points of inflection at 50 mol. % of urea are evidence of a compound with a composition of $CO(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$, i.e., the same compound that was found by the fusibility method.

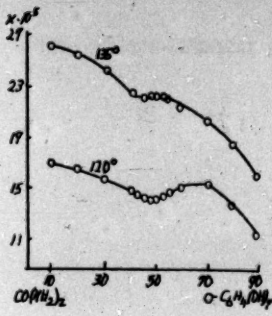

Fig.10.

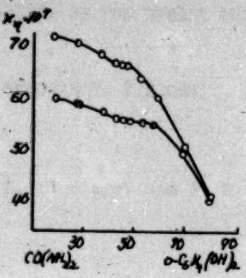

Fig.11.

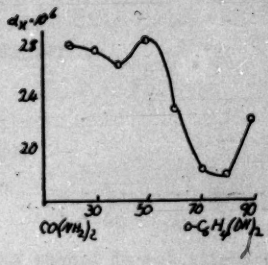

Fig.12.

SUMMARY

1. The viscosity, density, and conductance of the urea – phenol and urea – pyrocatechol systems have been determined at 120 and 135°.

2. No chemical interaction has been detected in the urea – phenol system.

3. The components have been found to interact in the urea – pyrocatechol system, and the existence of the equimolecular compound $CO(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$, has been proven.

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THE PHYSICO-CHEMICAL ANALYSIS OF THE BINARY SYSTEMS OF UREA AND THE PHENOLS

II. CONDUCTANCE, VISCOSITY, AND DENSITY

D. E. Dionisyev and N. Z. Rudenko

In our preceding paper [1] we showed that urea and phenol do not interact in the liquid phase and that the curves of the properties studied do not confirm the existence of the compound $CO(NH_2)_2 \cdot 2C_6H_5OH$ established by the fusibility method. In the urea – catechol system, however, the formation of the compound $CO(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$, is corroborated. Pursuing our investigation, we have made a study of the conductance, viscosity, and density of the following systems: urea – resorcinol and urea – hydroquinone.

As in our previous paper [1], we measured the conductance in a closed vessel with smooth platinum electrodes, the internal friction in a closed Ostwald viscosimeter, and the density in a Regnault pyknometer.

The Urea – Resorcinol System

Viscosity was measured at 120 and 135°. The measurement results are listed in Table 1, while the curves of viscosity as a function of concentration, expressed in molar per cent, are plotted in Fig. 1.

TABLE 1

No.	Mol. % $CO(NH_2)_2$	Viscosity $\eta \cdot 10^3$		No.	Mol. % $CO(NH_2)_2$	Viscosity $\eta \cdot 10^3$	
		120°	135°			120°	135°
1	90	-	29.1	7	45	60.2	40.8
2	80	39.0	31.0	8	40	60.1	41.2
3	70	46.6	34.8	9	35	60.0	41.2
4	60	52.9	38.0	10	30	59.7	41.0
5	55	57.5	38.9	11	20	59.0	40.5
6	50	59.9	39.9	12	10	58.5	39.8

As we see in Fig.1. the viscosity isotherms rise steeply from the less viscous urea, passing through a moderate maximum and dropping along an almost straight line to the viscosity of resorcinol. On the 120° isotherm the maximum is located at about 45 mol. % of urea, shifting toward the more viscous component as the temperature is raised. The shape of the viscosity isotherms indicate that chemical interaction between the components takes place within the system. The absolute temperature coefficient of viscosity has been calculated (Table 2). Its curve (Fig.2) exhibits a maximum located at 50 mol. % of urea.

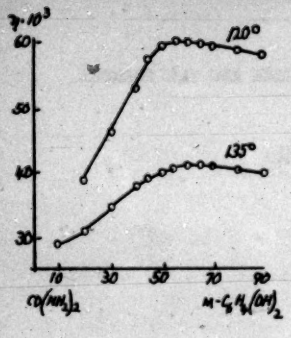

Fig.1.

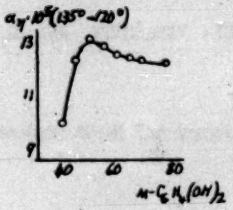

Fig.2.

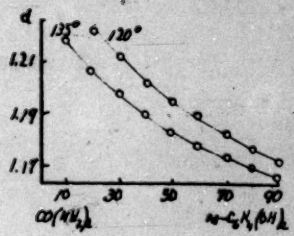

Fig.3.

TABLE 2

No.	Mol. % $CO(NH_2)_2$	Temperature coefficient of Viscosity $\eta \cdot 10^5$
1	80	5.33
2	70	7.87
3	60	9.25
4	55	12.4
5	50	13.3
6	45	12.9
7	40	12.6
8	35	12.5
9	30	12.4
10	20	12.3

TABLE 3

No.	Mol. % $CO(NH_2)_2$	Density	
		120°	135°
1	90	-	1.2178
2	80	1.221	1.2063
3	70	1.2115	1.1976
4	60	1.2021	1.1900
5	50	1.1948	1.1840
6	40	1.189	1.1791
7	30	1.1783	1.1756
8	20	1.1740	1.1712
9	10	1.1735	1.1650

The curves plotted from the data in Fig. 3, showing the density as a function of the composition at 120 and 135° are reproduced in Fig. 3. They are slightly concave upward.

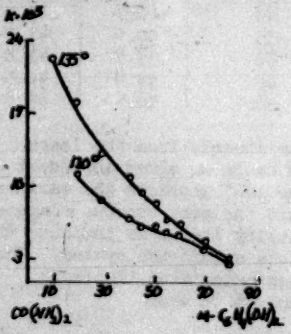

Fig. 4.

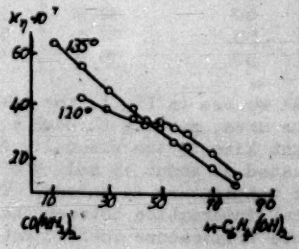

Fig. 5.

Conductance

Conductance was measured at the same temperatures as those used in the viscosity measurements. The conductance measurements are listed in Table 4, while the curves showing the variation of conductance with composition are reproduced in Fig. 4. As we see in Fig. 4, the conductance isotherm at 120° drops from the value of conductance for urea and exhibits a point of

Table 4

No.	Mol. % $CO(NH_2)_2$	Conductance $\chi \cdot 10^5$		No.	Mol. % $CO(NH_2)_2$	Conductance $\chi \cdot 10^5$	
		120°	135°			120°	135°
1	90	-	22.0	6	50	5.97	8.32
2	80	11.2	18.0	7	45	5.50	6.80
3	70	8.50	13.0	8	40	5.00	6.2
4	60	6.85	10.7	9	30	4.10	4.6
5	55	5.95	9.40	10	20	2.45	3.0

inflection at 50 mol. % of urea. Such an S-shaped conductance curve is common for systems in which chemical action occurs [3,4]. The 135° conductance isotherm is steady, not giving any direct indication of the presence of chemical action within the system.

The curves of "derived" conductance (Table 5 and Fig. 5) are similar, the 120° isotherm exhibiting a point of inflection and the 135° curve being monotonous and slightly concave upward.

TABLE 5

No.	Mol. % $CO(NH_2)_2$	$\chi\eta \cdot 10^7$	
		120°	135°
1	90	-	64.0
2	80	43.6	55.0
3	70	39.6	47.0
4	60	36.2	40.6
5	55	34.1	36.6
6	50	37.5	33.1
7	45	33.0	27.5
8	40	30.0	25.5
9	30	24.4	18.8
10	20	14.2	12.1

TABLE 6

No.	Mol. % $CO(NH_2)_2$	$\alpha_\chi \cdot 10^6$
1	80	30.9
2	70	28.0
3	60	29.3
4	55	30.0
5	50	22.0
6	45	14.2
7	40	14.3
8	30	7.70
9	20	13.4

We see that the coordination compound that disturbs the smooth course of the 120° isotherm disappears in the temperature interval from 120 to 135°.

The relative temperature coefficient of conductance is tabulated in Table 6, its curve as a function of composition being plotted in Fig. 6. The curve is quite complex, having a minimum as well as a maximum. The maximum is located

at 55 mol. % of urea. We are not inclined to consider all the singular points on the curve of the temperature coefficient of conductance as indications of the formation of a chemical compound, unless these indications coincide with the results secured by other methods [5].

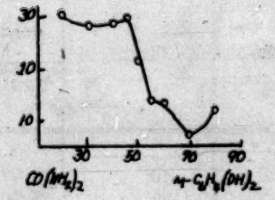

Fig. 6

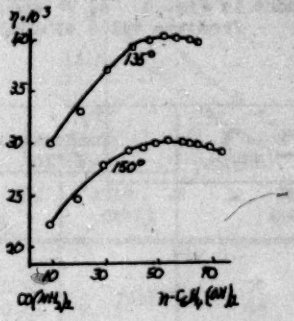

Fig.7.

The Urea - Hydroquinone System

An investigation of this system by the fusibility method disclosed the existence of a considerably dissociated chemical compound:

$$CO(NH_2)_2 \cdot n\text{-}C_6H_4(OH)_2.$$

In our research we used a hydroquinone with a m.p. of 171°.

Viscosity

The system's viscosity was measured at 135 and 150°, the measurements being listed in Table 7, and the curves of viscosity as a function of concentration being plotted in Fig. 7.

TABLE 7

No.	Mol. % $CO(NH_2)_2$	Viscosity $\eta \cdot 10^3$		No.	Mol. % $CO(NH_2)_2$	Viscosity $\eta \cdot 10^3$	
		135°	150°			135°	150°
1	90	30.2	22.1	7	45	41	30.5
2	80	33.2	24.5	8	40	40.6	30.4
3	70	37.5	27.9	9	37.5	40.4	30.3
4	60	39.8	29.4	10	35	-	30.2
5	55	40.4	29.6	11	30	-	30.2
6	50	41.4	30.2	12	25	-	29.6

The viscosity isotherms are curves that are concave downward, a maximum being located at 50 mol. % of urea at the lower temperatures. According to the generally accepted interpretation of viscosity isotherms [6], curves of this shape are evidence of chemical interaction within the system, with the maximum giving the approximate composition of the compound produced.

The temperature coefficient of viscosity was calculated (Table 8). The curve showing how it varies with composition (Fig. 8) has a maximum at 50 mol. % of urea.

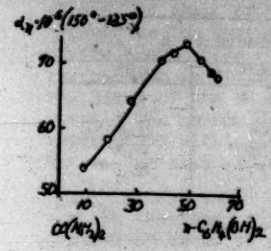

Fig. 8.

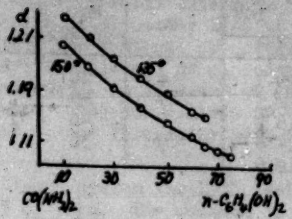

Fig. 9.

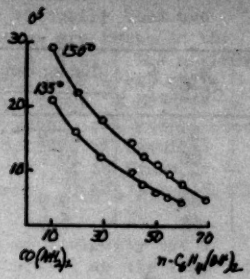

Fig. 10.

TABLE 8

No.	Mol. % $CO(NH_2)_2$	Temperature coefficient of Viscosity $\alpha \cdot 10^6$ (150-135°)
1	90	54.0
2	80	58.0
3	70	64.1
4	60	69.5
5	55	72.1
6	50	72.7
7	45	70.1
8	40	68.1
9	37.5	67.5

TABLE 9

No.	Mol. % $CO(NH_2)_2$	Density	
		135°	150°
1	90	1.2181	1.2072
2	80	1.2095	1.1990
3	70	1.2211	1.1901
4	60	1.1950	1.1840
5	50	1.1889	1.1780
6	40	1.1831	1.1723
7	35	1.1809	1.1699
8	30	-	1.1682
9	25	-	1.1665

The curves of density as a function of the concentration (Table 9 and Fig.9) at 135 and 150° are slightly concave upward.

Conductance

The conductance was measured at the same temperatures as the viscosity was, the results being tabulated in Table 10 and the curves of conductance as a function of concentration being plotted in Fig.10.

The conductance curves, which are slightly concave upward, are smooth, falling from the higher conductance of urea to that of hydroquinone. Curves of this sort, first observed for systems in which there was no chemical interaction [7], were later found to exist in system's exhibiting interaction between their components [4,5].

We then corrected the conductance for viscosity (Table 11 and Fig.11). This correction made the curves approach straight lines but did not affect their smooth course. Neither the conductance isotherms nor the curves of the "corrected" conductance gave any direct evidence of the existence of chemical interaction within the system.

Table 12 lists the results of our computation of the temperature coefficient

TABLE 10

No.	Mol. % $CO(NH_2)_2$	Conductance $\underline{x} \cdot 10^5$		No.	Mol. % $CO(NH_2)_2$	Conductance $\underline{x} \cdot 10^5$	
		135°	150°			135°	150°
1	90	20.9	29.1	6	50	7.1	11.3
2	80	16.2	22.5	7	45	6.4	9.6
3	70	12.1	18.0	8	40	5.89	8.4
4	60	9.9	14.6	9	30	-	6.1
5	55	8.51	12.6				

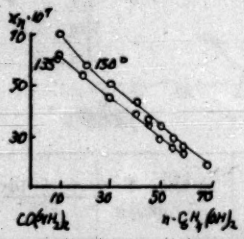

Fig.11.

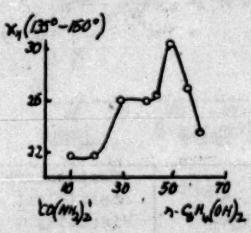

Fig.12.

of conductance, it being plotted as a function of concentration in Fig.12.

The shape of the curve is complicated. We find two maxima and two minima, one of the maxima (the higher one) being located at 50 mol. % of urea.

TABLE 11

No.	Mol. % $CO(NH_2)_2$	Conductance times viscosity $\underline{x}\eta \cdot 10^7$	
		135°	150°
1	90	63.0	64.2
2	80	53.9	56.0
3	70	45.4	50.2
4	60	39.2	43.0
5	55	34.5	36.2
6	50	29.1	34.4
7	45	26.2	25.5
8	40	23.9	18.4
9	30		

TABLE 12

No.	Mol. % $CO(NH_2)_2$	Temperature coefficient of conductance $\alpha_{\underline{x}} \cdot 10^6$
1	90	21.8
2	80	21.7
3	70	26.2
4	60	25.7
5	55	26.0
6	50	30.5
7	45	26.7
8	40	23.5

Evaluation of Results

The viscosity isotherms of the urea – resorcinol system exhibit a maximum at about 45 mol. % of urea, which is shifted toward the more viscous component as the temperature is raised. The conductance isotherm at 120° does not have quite the usual S-shaped course, its point of inflection lying at 50 mol. % of urea. As the temperature is raised, the 135° isotherm assumes the shape of a curve that is

slightly concave upward. Correcting the conductance for viscosity does not affect the shape of the curves. S-shaped conductance curves are known in the literature for systems in which chemical interaction occurs [3,4]. The maximum of the temperature coefficient of viscosity lies at 50 mol. % of urea, while the maximum is displaced from the rational composition to 55 mol. % of urea on the curve of the temperature coefficient of conductance, which is a complicated curve. The course of these curves is evidence of the existence of chemical interaction within the system. The composition of the compound is found to be the same as that established by the fusibility method, namely $CO(NH_2)_2 \cdot m\text{-}C_6H_4(OH)_2$.

In the urea – hydroquinone system the 135° isotherm of viscosity has a maximum at about 50 mol. % of urea. The maximum is obliterated as the temperature is raised. The temperature coefficient of viscosity exhibits a clearly marked maximum at 50 mol. % of urea. The temperature coefficient of conductance is a complicated curve, one of its maxima being located at 50 mol. % of urea. The course of these curves is evidence of the existence of chemical interaction within the system. The composition of the resultant compound $CO(NH_2)_2 \cdot n\text{-}C_6H_4(OH)_2$ is the same as that established by the fusibility method. The smooth conductance isotherms, as well as those of the "corrected" conductance give no indication of the chemical interaction occurring within the system.

SUMMARY

1. A study has been made of the viscosity, density, and conductance of the following systems: urea – resorcinol at 120 and 135°, and urea – hydroquinone at 135 and 150°.

2. Chemical interaction of the components has been found to exist in the urea – resorcinol system. The compound $CO(NH_2)_2 \cdot m\text{-}C_6H_4(OH)_2$ is formed.

3. Chemical interaction between the components has been found to exist in the urea – hydroquinone system. The existence of the compound $CO(NH_2)_2 \cdot n\text{-}C_6H_4(OH)_2$ has been established. This interaction is not shown on the conductance isotherms.

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*See page 59, C.B. English translation.
**See page 1217, C.B. English translation.
***See page 1223, C.B. English translation.

THE SOLUBILITY OF COPPER, SILVER, AND MERCURY ACETYLIDES

A. K. Babko and M. I. Grebelskaya

The methods of determining acetylene in the control of various production processes chiefly involve the formation of the slightly soluble acetylides of copper, mercury, and silver; however, no research has been done on the solubility of these acetylides, which complicates the choice of a precipitating agent and of appropriate reaction conditions. The scattered data in the literature give rise to doubt whether it is basically possible to employ some of these precipitates. It is stated, for example, that mercurous acetylide is decomposed by potassium cyanide, while, on the other hand, the use of an alkaline solution of mercuric cyanide to effect quantitative precipitation of acetylene is described.

The most important general characteristic of precipitates is their solubility product. Once we know the nature of the equilibrium between the solid phase and the solution, together with the numerical value of the precipitate's solubility product, we can select a reagent and forecast the course of the reaction under various conditions. The solubility product principle has been employed hitherto for the usual precipitates, which are salts of strong electrolytes; moreover, the acetylides of the metals exhibit significant peculiarities. The well-known researches of A. N. Nesmeyanov [1] have shown that in some reactions addition products of the $HgCl_2 \cdot C_2H_2$ type behave like coordination compounds and in others like organometallic compounds. Similarly, C_2Hg, mercurous acetylide, where the metal is directly linked to the carbon, behaves like an ordinary salt of the acid C_2H_2 in reactions with acids and in other reactions. The properties of acetylene as an acid are involved in another singularity of the acetylides. There are several references in the literature to the absence of any perceptible acidic dissociation of acetylene in aqueous solutions.

Our experiments have shown that the solubility of acetylene in water and in water-alcohol mixtures is not increased (within the margin of experimental error) by the presence of an alkali, i.e., no formation of even a highly hydrolyzed salt of the alkali metal is observed. We know [2] that acetylene displaces ammonia in amides of the alkali metals. Comparing this reaction with the well-known complete decomposition of calcium carbide by water, we may write:

$$2MeNH_2 + C_2H_2 = 2NH_3 + C_2Me_2;$$
$$C_2Me_2 + 2HOH = C_2H_2 + 2MeOH.$$

Therefore, the constant of acidic dissociation of C_2H_2 must be less than 10^{-14} (K_{H_2O}), and more than the constant of acidic dissociation of ammonia. The value of the latter is known to be [3]:

$$K_{NH_3} = \frac{[NH_2^-] \cdot [H^+]}{[NH_3]} = 1.9 \cdot 10^{-33}.$$

But determining the dissociation constants directly is impossible for acids whose dissociation is less than that of water. In the light of the peculiarities cited above, a study of the solubility of metal acetylides is of interest in the theory of precipitates, in addition to its practical importance. The present paper reports on an experimental investigation of the solubility of the acetylides of copper, silver, and mercury in acids, the influence of an excess of the precipitating agent, and the reactions of the acetylides with various anions that react with Cu^+, Ag^+ and Hg^{++}. Our results have been processed in accordance with the general theory of precipitates, applying to usual precipitates of the electrolyte type, with allowances made for the singularities of acetylides mentioned above.

The expression for the solubility product has a simple physical meaning for most of the common precipitates, representing the concentration of the ions in direct equilibrium with the precipitate. But a third component, the H^+ or OH^- ions, begins to play an extremely important part in the precipitate – solution equilibrium even in some well-known precipitates. We find, for example, from the second dissociation constant of hydrogen sulfide, $K^{II}_{H_2S} = 10^{-15}$ that the $[S^{--}]:[HS^-]$ ratio is $\frac{[S^{--}]}{[HS^-]} = \frac{K^{II}_{H_2S}}{[H^+]} = \frac{10^{-15}}{10^{-14}} = \frac{1}{10}$. even in a highly alkaline solution (at a pH of 14).

Sulfides are therefore hydrolyzed 90% or more even in strongly alkaline solutions. That is why the equilibrium:

$$MeS_{(solid)} \rightleftarrows Me^{++} + S^{--} \qquad (1)$$

never applies to sulfides.

Even in strongly alkaline solutions the equilibrium between the solution and the precipitate is governed chiefly by hydrolysis:

$$MeS\ (solid) + HOH \rightleftarrows Me^{++} + HS^- + OH^-. \qquad (2)$$

As we know, the equilibrium: $MeS\ (solid) + 2H^+ \rightleftarrows Me^{++} + H_2S$ has been investigated experimentally for metal sulfides.

Once we know the quantities

$$K_{equil.} = \frac{[Me^{++}]\ [H_2S]}{[H^+]^2} \text{ and } K_{H_2S} = \frac{[H^+]^2\ [S^{--}]}{[H_2S]} \qquad (3)$$

we can calculate the solubility product $L_p = K_{equil.} \cdot K_{H_2S}$. The expression giving the L_p for sulfides indicates the energy of the chemical bond between the Me^{++} and S^{--} ions during the formation of the precipitate, but it does not reflect the process itself, which always involves a third component: the H^+ ions. This singularity is of even greater importance for the acetylides.

We know that the usual acetylides are completely decomposed by water. The acetylides that are coordination compounds (compounds of Hg^{++}, Ag^+, and Cu^+) are not affected by water, though the equilibrium of a saturated solution must resemble Equation (2):

$$C_2Me_2\ (solid) + 2HOH \rightleftarrows 2Me^+ + C_2H_2 + 2OH^-. \qquad (4)$$

The acidic dissociation constant $K_{C_2H_2} = \frac{[H^+]^2\,[C_2^{--}]}{[C_2H_2]}$ is unknown for C_2H_2 (nor can it be determined directly), so that we cannot calculate $L_p = [Me^+]^2[C_2^{--}]$.

Thus the only difference between the acetylides and the sulfides is that we know the values of K_{H_2S} for the latter, so that we calculate (but not determine directly) the value of L_p; this in turn enables us to place the sulfides on the same footing as ordinary precipitates. Both the metal sulfides and the metal acetylides (plus some other precipitates) must, at bottom, be classed as a special group of precipitates, a saturated solution of which is not characterized by the usual equilibrium with the ions of the precipitate itself, but by the "hydrolytic solubility." The lack of data on the acidic dissociation of acetylene and the special nature of the equilibrium between acetylide precipitates and water cannot, of course, interfere with the quantitative description of all the properties of the sparingly soluble acetylides. Using Equation (4), which corresponds most closely to the actual equilibrium, makes it possible to allow for various singularities of the precipitation and dissolution of the acetylides. It becomes easy, for instance, to explain the seeming contradiction mentioned at the outset of this paper in the data on the course of the reaction in the system consisting of Hg^{++}, CN^{--}, and acetylene.

The properties of a certain group of precipitates, discussed above, justifies our using the term "hydrolytic solubility product" or "hydrolysis product" to characterize the acetylides; we shall denote this product henceforth by L_h. Thus, we get:

$$L_h = [Me^+]^2[C_2H_2][OH^-]^2. \qquad (5)$$

for a C_2Me_2 precipitate. This expression indicates that the solubility of acetylides definitely depends upon the concentration of the metal ions, the acetylene concentration, and the pH of the solution.*

The Solubility of Acetylides in Acids

An experimental check of the solubility of acetylides in acids is of basic importance to corroborate the applicability of the expression for L_h. Moreover, increasing the acidity of the solution makes it possible to increase the solubility of acetylides that are only very slightly soluble to values that may be reliably determined by the usual experimental methods. Lastly, it is obvious that data on solubility in acids are of direct interest practically in selecting the conditions of precipitation.

The acetylides were prepared under the conditions ordinarily employed to precipitate them in the determination of acetylene. The acetylene was prepared from calcium carbide and purified by passing it through solutions of iodine and thiosulfate. Cuprous acetylide was precipitated from an ammoniacal solution of copper sulfate with a large excess of hydroxylamine hydrochloride present. Silver acetylide was prepared by precipitation from a coordination compound of silver

*If the acidic dissociation constant of acetylene $C_2H_2 \rightleftharpoons 2H^+ + C_2^{--}$, should be calculated at some future date by some indirect method or other, it will be easy to calculate the quantity $L_p = [Me^+]^2[C_2^{--}]^2$ from the equation

$$L_p = L_h \frac{K_{C_2H_2}}{K^2_{H_2O}}.$$

and ammonia, while mercuric acetylide was prepared by passing acetylene through an alkaline solution of mercuric oxide in potassium iodide. The resultant acetylides were washed repeatedly and then placed in bottles and stored under water. Steps were taken to prevent any acetylene from escaping during the determination of solubility.* Measures were also taken to protect the cuprous acetylide against oxidation. This was done by filling the bottles in which the acetylide solubility was determined up to the top with solution, so as to keep all air bubbles out of the bottles. This absence of air inside the bottle made it much harder to stir the liquid, so that the bottle was not attached firmly to the mechanical agitator, but was syspended from it (by rubber tubing). After the solution had been saturated, it was filtered (or it was taken up directly into a pipet through a filtering layer of paper or asbestos); then the liquid was concentrated and its metal content was determined by the usual methods of volumetric analysis.

The results of our experiments on the solubility of silver acetylide are listed in Table 1.

TABLE 1

Solubility of C_2Ag_2 in Acids

No.	Acid	Concentration Of H^+ ions used	Concentration of Ag^+ ions (found)	$L_h C_2Ag_2$ $L_h=[C_2H_2][Ag^+]^2[OH^-]^2$
1	$HClO_4$ . . .	1.0	$2.10\cdot10^{-3}$	$4.5\cdot10^{-37}$
2	$HClO_4$ . . .	10^{-1}	$0.38\cdot10^{-3}$	$2.7\cdot10^{-37}$
3	HNO_3 . . .	1.0	$2.60\cdot10^{-3}$	$8.7\cdot10^{-37}$
4	HNO_3 . . .	10^{-1}	$0.46\cdot10^{-3}$	$4.8\cdot10^{-37}$
5	H_2SO_4 . . .	1.0	$1.26\cdot10^{-3}$	$1.0\cdot10^{-37}$
6	H_2SO_4 . . .	10^{-1}	$0.28\cdot10^{-3}$	$1.1\cdot10^{-37}$
7	CH_3COOH . .	$4.2\cdot10^{-3}$	None found	–

The last column of the table lists the results of calculations of the hydrolytic solubility product, L_h, for C_2Ag_2. When the extremely small size of the quantity L_h is borne in mind, the agreement of the results may be regarded as satisfactory. The slightly lower value of solubility in sulfuric acid is due to the fact that in our calculation we assumed that the H_2SO_4 is fully dissociated. The variation of solubility with acid concentration (for each of the acids) is characteristic. Changing the acid concentration by a factor of 10 causes a change in solubility by a factor of 5 to 5.4. The equation:

$$C_2Ag_{2(solid)} + 2HOH \rightleftarrows C_2H_2 + 2Ag^+ + 2OH^-, \qquad (5a)$$

may be used to calculate the solubility (taking x as the concentration of $[Ag^+]$):

* The solubility of acetylene in water is not high, totaling only 1.18 gram per liter at 18°, even when its vapor pressure is 1 atmosphere.

$$L_h = x^2 \cdot 0.5x \cdot [OH^-]^2 = 0.5x^3 \cdot [OH^-]^2.$$

It follows that a change of 1000% in the concentration of OH^- (or H^+) ions should cause the solubility x to change by a factor of $n = \sqrt[3]{10^2} = 4.6$, which agrees satisfactorily with the results listed in Table 1.

The results secured for cuprous acetylide (Table 2) exhibit a much less satisfactory agreement.

TABLE 2

Solubility of C_2Cu_2 in Acids

No.	Acid	Concentration of H^+ ions used	Concentration of Cu^+ ions (found)	$L_h C_2Cu_2$ $L_h=[C_2H_2][Cu^+]^2[OH^-]^2$
1	HNO_3 . . .	1.0	$1.3 \cdot 10^{-3}$	$1.2 \cdot 10^{-37}$
2	HNO_3 . . .	10^{-1}	$1.1 \cdot 10^{-3}$	$6.7 \cdot 10^{-36}$
3	H_2SO_4 . .	1.0	$1.3 \cdot 10^{-3}$	$1.2 \cdot 10^{-37}$
4	H_2SO_4 . .	10^{-1}	$1.0 \cdot 10^{-3}$	$2.8 \cdot 10^{-36}$
5	CH_3COOH .	$4.2 \cdot 10^{-3}$	$0.50 \cdot 10^{-3}$	$3.8 \cdot 10^{-34}$
6	CH_3COOH .	$1.3 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$1.2 \cdot 10^{-33}$

We might have supposed that this was due to mechanical contamination of the precipitate or to adsorption of copper at the surface of the C_2Cu_2 ions. Experiments to determine solubility, using various quantities of the precipitate yielded nearly identical results, however. A certain lack of agreement among the values for cuprous acetylide is rather due to the fact that the C_2Cu_2 precipitate always contains a certain quantity of divalent copper. The presence of Cu^{++} in the precipitate was proved by tests of the solubility of cuprous acetylide in ammonia. These tests yielded values of solubility that approached those for solubility in acetic acid, though the solutions were always colored a perceptible blue. The solubility of cuprous acetylide in acetic acid is lower than in strong acids, but higher than the theoretical value (if we take the expression for L_h as our starting point). In addition to the factors mentioned above, the formation of slightly dissociated copper acetates may also play a part. The solubility of C_2Cu_2 in hydrochloric acid is about 30 times as high as in nitric or sulfuric acid. This is doubtless due to the formation of copper chloride complex ions, the solubility of copper acetylide is also raised by the introduction of sodium chloride into the solution. Notwithstanding the discrepancies in our results, the data in Table 2 indicate, in general, that the L_h of C_2Cu_2 is higher than that of C_2Ag_2. This is fully borne out by the subjoined experiments on the order of solubility of the acetylides. Similar findings that cuprous acetylide has a higher solubility than silver acetylide were secured by Strizhevsky, who calculated $L_{C_2Cu_2}$ and $L_{C_2Ag_2}$ by an indirect method (making no allowance for hydrolysis), based on the concentration ratios of the acetylides and the soluble salts of copper and silver at the instant of equilibrium.

Our investigation of mercuric acetylide disclosed an infinitesimal solu-

bility of the precipitate. In the absence of ions that form coordination compounds, treatment with acids (H_2SO_4, HNO_3, CH_3COOH) did not cause any determinable quantities of mercury to enter solution. A tiny, though reliably measurable, solubility was detected when the precipitate was treated with hydrochloric acid, which is doubtless due to the formation of coordinated mercury chloride complex ions: $HgCl_4^{--}$ or $HgCl_3^-$. Calculations based on the assumption that either of these two complex ions is formed yield a solubility of about this order of magnitude. We believe it is more likely that $HgCl_3^-$ is formed, since a complex mercury ion with a coordination number of 4 (HgI_4^{--}) is formed, as we know, only at high iodide concentrations, even in the more stable mercury iodide complex ions. The dissolution reaction may be represented by the equation:

$$C_2Hg_{(solid)} + 2H^+ + 3Cl^- = HgCl_3^- + C_2H_2. \qquad (6)$$

The mercury in solution was determined iodometrically after it had been reduced with formaldehyde in an alkaline medium (with KI present); the solubility found experimentally (Table 3, Column 4) corresponds to the overall mercury concentration, i.e., the concentration of the complex ion $HgCl_3^-$. The expression:

$$K_{HgCl_3} = \frac{[Hg^{++}][Cl^-]^3}{[HgCl_3^-]} = 10^{-16}.$$

may be used to calculate the concentration of free mercury ions. The value 10^{-16} is taken from Abegg's findings, as well as from our calculations [4]. The concentration of the $[Cl^-]$ ions is known from the experimental conditions, while that of the $[HgCl_3^-]$ is determined experimentally.

TABLE 3

Solubility of C_2Hg in Acids

No.	Acid	Concentration of H^+ ions used	Solubility (overall mercury concentration)	$L_h C_2Hg$ $L_h=[C_2H_2][Hg^{++}][OH^-]^2$
1	HCl	1.0	$1.0 \cdot 10^{-3}$	$1 \cdot 10^{-50}$
2	HCl	10^{-1}	$4.6 \cdot 10^{-5}$	$2 \cdot 10^{-48}$
3	HNO_3 . . .	1.0	None found	–
4	H_2SO_4 . . .	1.0		–
5	CH_3COOH . .	$4.2 \cdot 10^{-3}$	" "	–

The concentration of $[Hg^{++}]$ ions thus found is substituted in the expression:

$$L_h = [Hg^{++}][C_2H_2][OH^-]^2. \qquad (6a)$$

We know the concentration of OH^- ions from the experimental conditions, while (6) indicates that the acetylene concentration equals the overall mercury concentration determined experimentally: $[C_2H_2] = [HgCl_3^-]$. The values of L_h for mercuric acetylide thus calculated are listed in the last column of Table 3.

As we see in Table 3, calculating L_h for mercuric acetylide yields values that are somewhat divergent; in view of the extraordinarily small order of magnitude of this quantity, even minute side reactions affect the computational results considerably.

The Solubility Series of the Acetylides

The solubility of cuprous, silver, and mercuric acetylides are given above, as well as calculations for the hydrolytic solubility products of these precipitates. These values of L_h enable us to arrange the foregoing acetylides in the following order of solubilities:

$$C_2Cu_2 > C_2Ag_2 > C_2Hg. \qquad (7)$$

We were interested in making an experimental check of the applicability of the law of series [5] generally adopted for other precipitates to the acetylides in order to confirm this order of the values of L_h.

Cuprous acetylide. The red-brown precipitate of C_2Cu_2 turns black when treated with a solution of $AgNO_3$. After having been agitated for 2 hours with an excess of 0.05N $AgNO_3$, the precipitate was filtered out and washed. Cu^{++} was detected in the solution, nothing but silver being found in the precipitate. Thus, the reaction:

$$C_2Cu_{2(solid)} + 2Ag^+ = C_2Ag_{2(solid)} + 2Cu^+, \qquad (8)$$

goes to completion, being governed, not by adsorption, but by the ratio between the L_h of the precipitates, in conformity with the results obtained above. The monovalent copper produced as the result of Reaction (8) was oxidized by the excess $AgNO_3$, yielding metallic silver and Cu^{++}. The red-brown precipitate of C_2Cu_2 turns white when treated with a 0.05N solution of $HgCl_2$. The exchange is complete in this case, too, nothing but mercury being found in the precipitate (no copper being detected).

Silver acetylide. The white precipitate of C_2Ag_2 did not change color when treated with an ammoniacal solution of monovalent copper. No copper was detected in the precipitate, while no silver was found in the solution. Thus, in conformity with the relative values of L_h derived above, Reaction (8) does not go to the left, even when a large excess of Cu^+ is present. Nor is the color of the precipitate changed when the C_2Ag_2 is treated with a solution of $Hg(NO_3)_2$, nothing but mercury being found in the precipitate and nothing but silver in the solution. These tests likewise serve as full confirmation of the ratios derived above.

Mercuric acetylide. No change in color is observed when the white precipitate of C_2Hg is treated with solutions of Cu^+ or Ag^+ salts, nor is copper or silver detected in the solid phase.

Hence, all the experiments described above confirm that the direction in which the reaction will go during the formation and dissolution of acetylides may be predicted from the general theory of precipitates and in conformity with the values we have found for L_h.

Effect of an Excess of the Precipitating Agent

One of the principal corollaries of the solubility product principle, as we know, is that of the effect of like ions upon the solubility of the precipitate. Three components are formed in the hydrolytic dissolution of acetylides: ions of the metal, molecules of C_2H_2, and OH^- ions. An increase in the concentration of any of these components ought to diminish the concentration of the other two accordingly. If the general postulates of the theory of precipitates are applicable to the acetylides notwithstanding their chemical singularities, this effect ought to exist. This is of considerable importance in selecting the conditions required for determining acetylene. The effect of an excess of the metal ion or of acetylene can be studied experimentally only in an acidic medium. At high values of pH, the solubility of the acetylides of copper, silver, and mercury is too low (provided there are no other forms of interaction present, such as the formation of new precipitates or of complex ions) to make the quantitative determination of solubility dependable.

We cite below our experiments on the change in the solubility of silver acetylide in 1N sulfuric acid produced by the addition of an excess of $AgNO_3$ or of acetylene to the solution. After the solution had been saturated, it was filtered and concentrated with HNO_3, and the silver was determined by titration. In the former case (with an excess of Ag^+ present), the increase in the percentage of silver in the solution due to the dissolution of the C_2Ag_2 depended upon the acetylene. We see from Equation (5a) that when the solution pH is constant:

$$[Ag^+]^2[C_2H_2] = \text{const.}$$

An excess of silver ions must therefore sharply reduce the solubility of the precipitate, while an excess of acetylene will lower solubility much less. The results of our tests, reproduced in Fig. 1, bear out this conclusion.

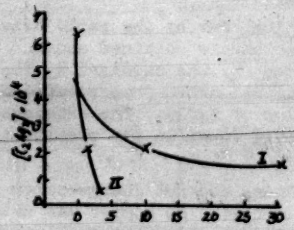

Fig. 1. Solubility of silver acetylide in 1N H_2SO_4 with an excess of the precipitant present.

I – Excess $[C_2H_2]\cdot 10^3$;

II – Excess $[Ag^+]\cdot 10^3$.

The pH has a profound effect upon the solubility of the acetylides. The variation of solubility with pH in an acid medium has been discussed earlier. At a pH > 7 the solubility of acetylides is so small (in accordance with the L_h) as not to be measurable directly. Several tests have confirmed that this also holds good, in conformity with the L_h, in an alkaline medium. Let us consider, by way of example, the reaction of silver acetylide with potassium iodide.

This reaction may be represented schematically* as follows:

*A more detailed investigation, on the basis of which we have evolved an acidimetric method for determining acetylene, shows that a soluble iodide complex ion of the AgI_2^- type is formed when C_2Ag_2 is treated with a concentrated solution of KI.

$$C_2Ag_{2(solid)} + 2I^- + 2H_2O \rightleftharpoons 2AgI_{(solid)} + C_2H_2 + 2OH^-. \quad (9)$$

The constant of this equilibrium is:

$$K_{equil.(9)} = \frac{[C_2H_2][OH^-]^2}{[I^-]^2} = \frac{L_h}{L^2_{AgI}} = \frac{4\cdot10^{-37}}{(10^{-16})^2} = 4\cdot10^{-5}. \quad (10)$$

If we treat silver acetylide with a 1N solution of potassium iodide, evidently $[I^-] = 1$ and $[OH^-] = 2[C_2H_2]$. Bearing in mind (10), we get:

$$4[C_2H_2]^3 = 4\cdot10^{-25}, \quad (11)$$

whence:

$$[C_2H_2] = 2.2\cdot10^{-2} \quad (11a)$$

(if the formation of the complex ion AgI_2^- is borne in mind, we get an even higher value). This value approaches the solubility of acetylene in water, so that we may expect the 1N solution of KI to decompose silver acetylide, yielding acetylene. This has been fully confirmed by experiment – when C_2Ag_2 is treated with a 1N solution of KI, acetylene is evolved vigorously and an equivalent quantity of alkali is formed. When silver acetylide is treated with 1N KI in the presence of an excess of alkali, say, at $[OH^-] = 1$, we get, in conformity with (10):

$$[C_2H_2] = K_{equil.}\frac{[I^-]^2}{[OH^-]^2} = K_{equil.} = 4\cdot10^{-5}. \quad (12)$$

Comparison of this value with (11a) shows that in the presence of an alkali the concentration of the acetylene evolved is much less than its solubility in water. As a matter of fact, silver acetylide is decomposed only very slightly indeed by potassium iodide when a 1N alkali is present. The ratio between the reacting components in the solution containing Hg^{++} and CN^- ions and acetylene is explained in a similar fashion. The equilibrium looks like this:

$$C_2Hg_{(solid)} + 4CN^- + 2H_2O \rightleftharpoons Hg(CN)_4^{--} + C_2H_2 + 2OH^-. \quad (13)$$

Taking the mean of the values of $L_h = 10^{-49}$ derived above for the solubility of C_2Hg, and the quantity:

$$K_{Hg(CN)_4^{--}} = \frac{[Hg^{++}][CN^-]^4}{[Hg(CN)_4^{--}]} = 10^{-42},$$

for the mercuric cyanide complex ion [6], we get:

$$K_{equil.(13)} = \frac{[Hg(CN)_4^{--}][C_2H_2][OH^-]^2}{[CN^-]^4} = \frac{L_h}{K_{Hg(CN)_4^{--}}} = \frac{10^{-49}}{10^{-42}} = 10^{-7}. \quad (14)$$

When mercuric acetylide is treated with a 1N solution of potassiam cyanide, the concentration of the reaction products: $Hg(CN)_4^{--}$, C_2H_2, and the OH^- ions, will then be x, x, and $2x$. In conformity with Equation (14), we get $4x^4 = 10^{-7}$, whence $x = [C_2H_2] = 1.3\cdot10^{-2}$, i.e., a value approaching the solubility of acetylene in water. As a matter of fact, the mercuric acetylide is decomposed by potassium cyanide, giving off acetylene. At first glance, this fact forces us to consider

one of the methods used for determining acetylene, based on precipitating it from an alkaline solution of mercuric cyanide, as completely unreliable. Further consideration of Equilibrium (13), however, leads us to another conclusion. For instance, let acetylene in a concentration (initial C_2H_2) of $0.25 \cdot 10^{-2}$ be added to a 0.1N solution of $K_2Hg(CN)_4$ in 1N KOH; then Reaction (13) will be shifted to the left to a large extent, and we get a concentration of $[CN^-]$ ions = 4 (initial C_2H_2) = 10^{-2} in the solution.* From Equation (14) we get:

$$[C_2H_2] = \frac{K_{equil.}\,[CN^-]^4}{[OH^-]^2[Hg(CN)_4^{--}]} = \frac{10^{-7} \cdot 10^{-8}}{10^{-1}} = 10^{-14},$$

i.e., the concentration of unreacted acetylene remaining in equilibrium with the alkaline solution of $K_2Hg(CN)_4$ will be negligible. Therefore, although C_2Hg is decomposed by potassium cyanide, an alkaline solution of mercuric cyanide is quite serviceable for the quantitative determination of acetylene, owing to the high concentration of hydroxyl ions.

The Reactions of Silver, Copper, and Mercury Acetylides With Various Reagents

We were interested in the behavior of the acetylides with various reagents that form precipitates or coordination compounds with Ag^+, Cu^+, and Hg^{++}, in order to learn the conditions governing the formation and decomposition of these acetylides. The following reagents were tested: Na_2S, KCN, KI, KBr, KCNS, $K_4Fe(CN)_6$, $Na_2S_2O_3$, and NaCl. Wherever possible we computed the equilibrium concentration of the acetylene evolved when the respective acetylide was treated with each of these reagents. This calculation was performed by a method resembling that discussed above for the acetylides of mercury and silver. Wherever the dissociation constant of the respective complex ion, such as AgI_2^-, was known, we assumed that these complex ions were formed in the concentrated solutions of the respective reagents (a detailed discussion of these calculations would require too much space). A high concentration of acetylene secured in these calculations was evidence of the instability of the given acetylide under the stated conditions. The results of an experimental check, listed in the respective columns of Table 4, are in satisfactory agreement with the bulk of our calculations.

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*Should Equation (13) shift to the left to a small extent, the concentration of $[CN^-]$ ions would be even lower, which might facilitate the leftward course of the reaction still more.

TABLE 4

Reaction of the Acetylides of Silver, Copper, and Mercury with Various Anions

No.	Reagent	Reagent concentration, mol per liter	Cuprous acetylide		Silver acetylide		Mercuric acetylyde	
			Evolution of C_2H_2		Evolution of C_2H_2		Evolution of C_2H_2	
			Theoret. Mol./l.	Exper.	Theoret. Mol./l.	Exper.	Theoret. Mol./l.	Exper.
1	Na_2S	0.1	$6.0 \cdot 10^{+2}$	*	$8.7 \cdot 10^{+15}$	*	3.10^{+4}	*
2	KCN	0.1	$9.4 \cdot 10^{+4}$		$1.9 \cdot 10^{+4}$		$1.3 \cdot 10^{-3}$	
3	KI	1.0	$8.2 \cdot 10^{-5}$	No C_2H_2 found	$1.4 \cdot 10^{-2}$		$1.5 \cdot 10^{-5}$	
4	KBr	1.0	$5.5 \cdot 10^{-6}$		$1.1\ 10^{-4}$	Slight decomposition	$1.0 \cdot 10^{-7}$	
5	NaCl	1.0	$4.9 \cdot 10^{-6}$		$5.4\ 10^{-8}$		$4.5 \cdot 10^{-9}$	
6	KCNS	1.0	$2.6 \cdot 10^{-4}$		$4.5\ 10^{-5}$		$1.3 \cdot 10^{-7}$	
7	$Na_2S_2O_3$	1.0	–	C_2H_2 evolved	$6.7\ 10^{-3}$		–	No C_2H_2 found
8	$K_4Fe(CN)_6$	0.1	–	No C_2H_2 found	$1.0\ 10^{-6}$	No C_2H_2 found	–	

*$CuCu_2$ completely decomposed.

SUMMARY

It has been shown that the equilibrium of saturated solutions of the acetylides of mercury, silver, and copper is described by a hydrolytic solubility:

$$C_2Me_{2(solid)} + 2H_2O = 2Me^+ + C_2H_2 + 2OH^-.$$

This relationship may be expressed by the "hydrolytic solubility product":

$$L_h = [Me^+]^2[C_2H_2][OH^-]^2.$$

An experimental study has been made of the solubility of the acetylides of Hg^{++}, Ag^+, and Cu^+ in acids, and L_h has been calculated for $C_2Ag_2(4 \cdot 10^{-37})$, for $C_2Cu_2(3 \cdot 10^{-36})$, and for $C_2Hg(10^{-49})$.

The applicability of the series rule to the acetylides of copper, silver, and mercury has been tested. The effect of an excess of the equilibrium components: Me^{+n}, C_2H_2, OH^-, upon the hydrolytic solubility has been investigated experimentally, the results being in satisfactory agreement with the reagents.

A study has been made of the reaction of these acetylides with various anions that combine with the cation of the precipitate; it has been shown that the calculated stability of the acetylides is satisfactorily confirmed by experiment.

These results make it possible to apply the general theory of precipitates to the calculation and prediction of the practical conditions required for the precipitation and dissolution of acetylides, bearing in mind certain specific features of precipitates of this type.

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A CALORIMETER FOR MEASURING THE LATENT HEAT OF VAPORIZATION OF HIGHLY VOLATILE LIQUIDS AT VARIOUS TEMPERATURES

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The indirect methods of determining the latent heat of vaporization of liquids sometimes fail, so that a direct experimental determination is always preferable. In our literature, however, not enough work has been done on the procedures involved in direct determinations. The procedure we propose makes it possible to measure the latent heat of vaporization of highly volatile liquids at temperatures that range from room temperature to 100°, using only very small quantities of the substance (a few grams) and securing results with an accuracy of 1% though employing comparatively simple apparatus.

Method. Some 1 to 2 grams of the substance under test is placed in a glass ampoule of special design. The ampoule is then placed in a depression in a massive copper cylinder, which serves as the calorimeter. Evaporation is effected by passing air, previously heated to the temperature of the calorimeter, through the layer of liquid in the ampoule, the amount of liquid vaporized being determined by the weight of the ampoule before and after the test, which is run under adiabatic conditions. The change in the calorimeter's temperature during the run enables us to calculate the substance's heat of vaporization, provided we know the heat capacity of the calorimeter system. The latter is determined in special experiments, involving the supply of heat by an electric current. The principle on which the calorimeter employed in the present research is based is the same as that of the calorimeter previously described by one of the present authors [1] for determining the true heat capacity of solids and liquids. The same principle is employed in the calorimeter suggested by Swietoslawski [2] for measuring the heats of adsorption and vaporization of highly volatile substances. But in the Swietoslawski calorimeter vaporization takes place without the passage of a current of air through the substance. This greatly increases the length of the run (ranging from 3 to 8 hours, depending upon the volatile liquid involved), thus requiring extraordinarily close control of the calorimeter's heat losses if reliable results are to be secured. In the procedure

we suggest vaporization is speeded up by the passage of an air current, as stated above. Smith [3] was the first one to employ the blowing of air through the substance, and the blowing through of air has been used with great success in the well-known original method due to Vrevsky [4]. The theory of this method is set forth in detail in the papers by Goff and Hunter [5] and by Hunter and Bliss [6], who indicate what corrections have to be applied to the observed readings to allow for the interaction of the vapor molecules with the molecules of the air blown through. The total of these corrections do not exceed 0.1% of the observed values, however, and may be ignored in our case. It should be pointed out that in all the papers cited, where gas is passed through in order to speed up vaporization, large calorimeters are employed, which require large quantities of the substance under test. The details of our procedure are set forth below.

Calorimeter.

The calorimeter (Fig. 1) was a massive copper cylinder (a), 45 mm in diameter and 75 mm high with a slightly conical hole bored into it to hold the ampoule containing the test substance. The calorimeter was suspended by 3 strings inside a thin-walled brass shell (b), the cover of which was secured by 8 screws, a rubber gasket being used to ensure airtightness. The clearance between the wall of the calorimeter and the shell was 15 mm.

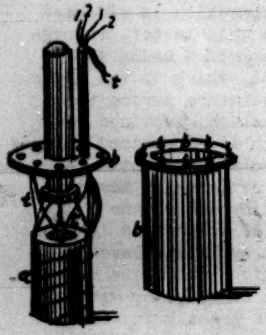

Fig. 1. Calorimeter and shell.

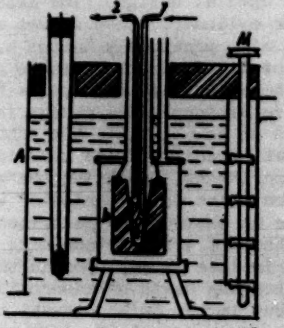

Fig. 2. Cross-sectional view of the calorimeter and its water jacket.

The shell and the calorimeter were placed on a special stand inside an outer jacket (A) (Fig.2) with a capacity of some 10 liters, which was filled with water. The water in this jacket was thoroughly stirred by a propeller stirrer (M), rotating at 1500 rpm. By adding hot water (from a boiler) or cold (from a water tap) to the jacket via special stopcocks, we were able to set up the desired temperature within the jacket and to maintain it to within 0.001-0.002°. In the tests run at 40° and 60° the jacket's heat losses were so high that we found it desirable to supplement the addition of hot water by supplying heat to the jacket via a heating coil of nichrome wire immersed in the water. The coil was arranged within the jacket in such a way as to ensure an even distribution of the heat throughout the jacket. The current passing through this coil was regulated so that the heat evolved compensated for nearly all the heat lost by the jacket to

the space surrounding it. Close regulation of the jacket temperature was achieved by adding hot or cold water in small quantities.

The temperature difference between the calorimeter and its water jacket was measured by the emf of a thermopile, consisting of 3 copper-constantan thermocouples (t), one junction of each of which was secured by Bakelite to the outer wall of the calorimeter, with the other junctions attached to the cover of the brass shell (Fig. 1). The emf of the thermopile was read off on a mirror galvanometer, whose voltage sensitivity was such that a calorimeter-shell temperature difference of 0.0003° could be read. This calorimeter design enabled us to gauge changes in its temperature from changes in the temperature of the jacket, without having to read the calorimeter's temperature. A preliminary test was made of the thermopile, so that we had complete certainty of there being no stray sources of emf in its circuit. The jacket temperature was measured with a Beckmann thermometer. Reading the thermometer in degrees, as well as any other correction to its reading, was rendered unnecessary by the fact that the heat capacity of the calorimeter system was measured in every case by the amount of heat supplied electrically, these tests being run, whenever possible at the same range of the thermometer's scale as that employed in the determination of the heat of vaporization.

To determine its heat capacity the calorimeter was equipped with a heating coil (c) (Fig. 1) - a manganin wire with a resistance of 10.5 ohms, affixed by means of Bakelite to (and electrically isolated from) the outer surface of the calorimeter. Each end of the heating coil was led outside through two copper leads (passing through a tube soldered to the cover of the shell). One pair of leads (1,1) served as a heating current supply, while the other (2,2) was used to measure the voltage across the end of the heating coil.

Ampoule for vaporizing the substance. The design of the glass ampoule is seen in Fig. 3. Its dimensions were such as to fit tightly within the hole bored into the calorimeter. Still greater tightness was secured by covering the side walls of the ampoule with several thicknesses of aluminum foil; this ensured good heat transfer between the ampoule and the calorimeter. Two glass tubes, attached by means of ground-glass joints, served the following purposes: one passed air into the ampoule through the layer of the substance (1), while the other (2) carried off the vapor to an absorber. Tube 2 was equipped with a bulb (3) to prevent any liquid condensing from the exhaust vapor from flowing back to the ampoule. When the ampoule was weighed before and after the run, the tubes were disconnected and replaced by ground-glass stoppers (4). A plug of glass wool was placed in the expanded section (5) to retain any liquid spray that might be carried along by the passage of air. The air passing through the layer of liquid in the ampoule must be first freed of dust, dried, and heated to the temperature of the calorimeter. Moreover, provision must be made for the fine adjustment of the rate of air flow, which must be held constant.

The design of the drying system is visible in Fig. 4, where 1 and 1 are large-capacity vessels to create pressure (since only little air was consumed in each test, the pressure could be regarded as constant), 2 is a vessel for observing the rate of air flow, 3 and 9 are micrometric regulating valves, and 4-8 are the absorbing bottles.

Before entering the calorimeter, the air passed through the drying system and then through a coil consisting of a thin-walled copper tube, 2 mm in diameter and 4 meters long. This coil was immersed in the water of the calorimeter jacket. Preliminary tests showed that tubing of this length made sure that the

air was warmed up completely at the flow rates employed. The air thus dried and warmed was passed through the layer of liquid under test in the ampoule placed within the calorimeter. The vapor of the substance was carried off through the tube 2 and condensed in a condenser or collected in appropriate receivers, depending upon the nature of the liquid.

Running the experiment. The test was run as follows. The ampoule containing the substance under test was first weighed to the nearest 0.1 mg and then packed tightly into the calorimeter. To prevent the liquid from evaporating during the preliminary test period, rubber tubing fitted over the ends of the ampoule tubes was closed off by clamps. The calorimeter (a) (Fig.1) was placed within the shell (b), the latter's cover was screwed down tight (gasket), and the shell was placed in the water jacket (A) (Fig. 2). The calorimeter suspension was so designed as to make it possible to lower the calorimeter to the bottom of the brass shell in order to speed up the attaining of thermal equilibrium between the calorimeter and the shell. As soon as equilibrium was established, the calorimeter was raised again, and the calorimetry test, consisting of initial, principal, and terminal periods as a rule, was run. The initial test period was run solely to determine the initial temperature of the calorimeter accurately. In the principal period, air that had been previously dried and warmed as described above was passed through the layer of substance in the ampoule, causing the temperature of the calorimeter to drop as a result of evaporation. To keep the test conditions adiabatic the temperature of the water jacket was lowered to the same extent (by adding cold water). We were able to run the test under such conditions that the required correction for incompletely adiabatic conditions was always less than 0.001° and could be ignored.

The substance was evaporated very slowly as a rule (0.4 – 0.5 g of the substance being evaporated within about 1 hour at 20°). The temperature of the calorimeter dropped by only 0.3 – 0.4° during the entire run. This eliminated any possibility of supercooling the liquid below the calorimeter's temperature, so that the process could be regarded as isothermal. The terminal period of the test involved the finding of the equilibrium temperature of the calorimeter after the run was over.

Determining the heat capacity of the calorimeter system. The heat capacity of the calorimeter system (including the ampoule and the test substance) was determined in special tests by electric heating. The same calorimetric test was made, the sole difference being that a previously fixed value of electric current was passed through the calorimeter heating coil during the principal test period instead of vaporizing the substance. Adiabatic conditions were ensured by adding hot water to the jacket. The amount of electric energy passing through the calorimeter heating coil was measured by means of the usual compensation circuit. The time during which the current flowed was measured by a stop watch. The stop watch and the instruments used to measure the electric energy were first checked to make sure that the overall absolute error in reading the electric energy could not exceed 0.05%. The relative accuracy of the tests could not exceed 0.5% owing to the extremely small temperature rise during the runs (0.3 – 0.4°).

Table 1 gives an example of the determination of the heat capacity of the calorimeter system at 40°.

TABLE 1

Heat Capacity of the Calorimeter System at 40°

Test No.	I	E	τ	Q	$\Delta\vartheta$	W	Mean value of W
20	0.14468	0.7060	311.7	20.33	0.282	72.1	
21	0.14051	1.6590	565.3	31.48	0.437	72.0	
23	0.14134	1.6692	419.3	23.63	0.331	71.4	71.7±0.5%
25	0.14100	1.6658	513.8	28.83	0.402	71.7	
35	0.21293	2.5161	245.6	31.43	0.442	71.1	

Notation: I – heating coil current, amperes; E – voltage across the heating coil, volts; τ – time in seconds; Q – amount of heat evolved by the current, calories; $\Delta\vartheta$ – rise of calorimeter temperature, standard degrees; W – heat capacity of the calorimeter system.

Fig. 3. Ampoule for vaporizing the substance.

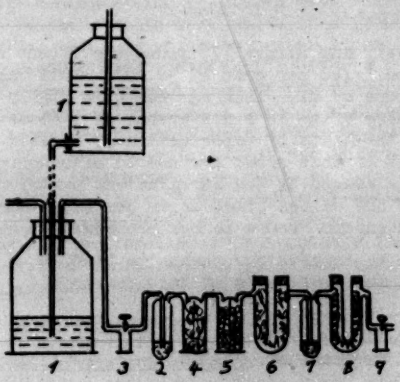

Fig. 4. Drying system.

Testing the procedure. Before investigating the heat of vaporization of the object under test, we felt it was necessary to check the procedure by determining the heat of vaporization of some substance that had been investigated already. We could not use water for this purpose, since its high heat of vaporization and low volatility would necessitate another type of calorimeter. The

only organic liquid of adequate purity at our disposal was toluene. We therefore had to employ it in this procedural check, notwithstanding the fact that the data in the literature on the heat of vaporization of toluene are extremely scanty. The results we secured for the heat of vaporization of toluene at 40° are given below (Table 2).

TABLE 2

Test No.	Grams of substance vaporized	Change in calorimeter temperature, standard degrees	Calorimeter heat capacity, calories/ standard degree	Heat of vaporization, calories/gram
1	0.3690	0.502	71.7	97.5
2	0.3412	0.459	71.7	96.4
3	0.2877	0.391	71.7	97.4
			Average	97.1±0.5%

Kolosovsky and Alimov [7] found the latent heat of vaporization of toluene to be 98.5 calories per gram at 42.85°. This value differs by only 1.4% from the value found by us. This agreement is highly satisfactory, when we bear in mind that there often is a difference of 3-5% between the figures given by various authors for the heats of vaporization of organic substances. It is unlikely that descrepancies of this order are due to methodological errors; it is more likely that they are caused by the insufficient purity of the substances tested. The agreement of the values cited above justifies our inferring that there are no significant systematic errors in our procedure.

We wish to express our thanks to Prof. M. M. Popov for his counsel during the planning and performing of this research.

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SULFANURYL CHLORIDE

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The acid with the structure of N≡SOOH, which is unknown at the present time, ought to possess physical and chemical properties that reflect its own peculiar singularities, though it ought to resemble cyanic acid in some respects. That is why the acid with the structure of N≡SOOH should be called sulfanic acid, by analogy with cyanic acid. It is very likely that sulfanic acid or its tautomer sulfimide are intermediate products in the amidation of carboxylic acids and in the synthesis of imidosulfamide [1].

Not a single derivative of sulfanic acid is known at the present time. It is the objective of the present research to secure either sulfanic acid or one of its derivatives and to investigate their properties.

Sulfimide, which is tautomeric with sulfanic acid and for which a better name would be isosulfanic acid, is likewise unknown, though some of its derivatives are known. Traube [2] assumed that he had secured the silver salt of sulfimide from the reaction products of sulfuryl chloride and ammonia, as well as from the products of the thermal decomposition of sulfamide. Traube secured other salts of "sulfimide" by double decomposition reactions with this silver salt. Hantzsch [3] has shown that Traube's salts were salts of a trimer of sulfimide, the so-called trisulfimide, which it would be better to call isosulfanuric acid, by analogy with isocyanuric acid. Hantzsch's efforts to secure free isosulfanuric acid met with failure. Decomposition of the silver salt was always accompanied by acidolysis, producing a small yield of imidosulfamide [3]. Reacting the silver salt of isosulfanuric acid with methyl iodide and benzoyl chloride, Hantzsch secured the respective trimethyl and tribenzoyl derivatives. Hantzsch also describes a sulfomelide analogous to cyamelide, but we can hardly consider his data on sulfomelide reliable, inasmuch as he was unable to secure sulfomelide in the crystalline state and his description of the experiments involved in the synthesis of sulfomelide is not notable for its clarity. Thus, only a few derivatives of isosulfanuric acid, difficult of access, are known at the present time, while not a single derivative of sulfanuric acid is known.

There were two possible ways of synthesizing derivatives of sulfanic acid: the thermal cleavage of sulfamide and its metallic derivatives in the expectation of securing the respective salts of sulfanic acid, as follows:

$$NH_2SO_2NH_2 \rightarrow N{\equiv}SOONH_4$$

$$NH_2SO_2NHNa \rightarrow N{\equiv}SOONa+NH_3,$$

and the thermal cleavage of trichlorophosphazosulfuryl chloride [4] in the expectation of securing sulfanyl chloride (the acid chloride of sulfanic acid) or its polymers (such as sulfanuryl chloride), as follows:

$$ClSO_2N{=}PCl_3 \rightarrow POCl_3+N{\equiv}SOCl \rightarrow (N{\equiv}SOCl)x.$$

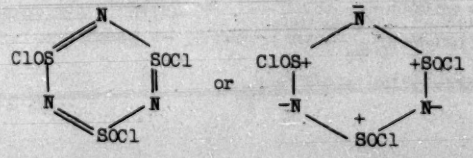
The latter reaction is similar to the thermal cleavage of esters as well as to the thermal cleavage of acylsulfamic acids [5]. It is highly probable that the synthesis of nitriles from the amides of carboxylic acid and phosphorus pentoxide likewise involves an intermediate stage of N-phosphoric acids, which are cleaved by heat into free phosphoric acid and the nitrile. There is, therefore an indisputable tendency for the liberation of a mineral acid in the free state or as an acid chloride, a salt, and the like, during thermal cleavages.

A rather large number of experiments have been performed on the thermal cleavage of sulfamide and of its metallic derivatives, but we have been unable as yet to find any derivatives of sulfanic acid among the decomposition products.

The second method proposed proved to be more successful. When trichlorophosphazosulfuryl chloride, with an m.p. of 32-33°, was heated in vacuum to 118-129°, about 0.92 mol of phosphorus oxychloride per mol of the acid chloride was used in the reaction. Hence, about 91% of the acid chloride was cleaved as indicated above, only some 8% decomposing without giving off phosphorus oxychloride. It is worthy of note that the crude acid chloride of trichlorophosphazosulfuric acid undergoes no change when heated as high as 137° under the same conditions. Apparently the crude product contains something that retards decomposition. Nor does decomposition occur at ordinary pressure, even when heated to 150°. As might have been expected the reaction product was not a homogeneous substance. In all probability the monomeric sulfanyl chloride undergoes further transformations, polymerization, in particular.

Two substances (α and β) were isolated from the reaction products, in addition to the phosphorus oxychloride. Moreover, it was shown indirectly that the reaction mixture contained at least three more substances (γ, δ, and ε), although these substances have not been isolated as yet. A feature of the substance ε is that when reacted with pure benzene or gasoline containing unsaturated compounds, it produces a bright golden-yellow color, which vanishes when the solvent is driven off in vacuum and reappears when the solvent is added. This substance is readily hydrolyzed by water. The substance is volatile, with a boiling point somewhat above 100° at an 8-mm vacuum. The yield of the ε substance was very small. It is quite possible that the ε substance is formed in equilibrium when one of the products is depolymerized by heat. Appreciable quantities of the substances γ and δ are produced. Both of them are hydrolyzed very readily. Substance δ is a liquid, distilling at 7 mm at about 125°, the yield being about 15.3% of the theoretical. Substance γ is a solid that apparently cannot be distilled in vacuum, is hydrolyzed with extreme ease at a temperature of about 10°, but can be suction-filtered from an aqueous mixture at 0°. The α and β substances were isolated as such, the yields being about 24% and about 18.5% of the theoretical, respectively.

Substance α contains no hydrogen or phosphorus, its composition being N≡SOCl, its molecular weight being equivalent to $(N{\equiv}SOCl)_3$. This leads us to believe that the molecular structure of the α susbstance is represented by the following formula:



This structure is also borne out by the fact that upon hydrolysis the substance yields 6 equivalents of acid without yielding any hypochlorous acid or active chlorine. Hence, the chlorine is linked to sulfur rather than to nitrogen. Thus the α substance is most likely the first known derivative of sulfanic acid, viz: a trimer of sulfanyl chloride. It may be called 1,3,5-trichloroxo-1,3,5-trithiatriazine or, by analogy with cyanuryl chloride, sulfanuryl chloride. It is worthy of note that sulfanuryl chloride fuses at 144.5-145.5°, while cyanuryl chloride has a m.p. of 146°, and that sulfanuryl chloride sublimes just as readily as cyanuryl chloride. The extent of the analogy between sulfanuryl and cyanuryl chlorides as far as their chemical properties are concerned will be set forth below.

Sulfanuryl chloride is hydrolyzed rather slowly by water. A sample weighing about 0.2 g, mixed with 30 ml of water, was hydrolyzed completely only after 45 minutes of continuous stirring at 90°. This may be due to the negligible solubility of the substance in water, since hydrolysis takes place very quickly when alcohol is added to the mixture. When a crystal of sulfanuryl chloride is placed on Congo paper and water is dropped on it, it takes some time for a blue spot to appear, but if the water contains a little alcohol, the blue spot appears immediately. Sulfanuryl chloride does not decompose when kept above sulfuric acid in a desiccator or kept in sealed ampoules, but it does react slowly with atmospheric moisture when stored under ordinary conditions, exhibiting a faintly acid reaction after a few hours have passed, while the vessel in which it was kept is found to contain gaseous hydrogen chloride. The m.p. of sulfanuryl chloride is 144.5-145.5° without decomposition; it distils at about 270°, though distillation usually ends with an explosion. When 0.4 g of sulfanuryl chloride was distilled at atmospheric pressure, for example, about half the substance distilled before an explosion occurred that sent the distilling flask and the receiver flying in little pieces. When sulfanuryl chloride is rapidly heated on a platinum spatula it is deflagrated in a very characteristic fashion, with a blue flame. Hydrogen chloride and sulfur dioxide are liberated. When 0.4 g of sulfanuryl chloride was heated over a small flame in an upright test tube, it boiled quietly for five minutes without any outwardly apparent decomposition, but then it exploded with a bright blue flash and a loud "hiss", the test tube escaping unscathed. Sulfur was deposited on the cooler upper walls of the test tube, and the strong odor of sulfur monochloride was perceptible. Sulfanuryl chloride sublimes readily when heated in vacuum, sublimation begining at 60° at a pressure of 0.5 mm, and being very rapid at 123-130°. The melting point of the sublimed substance is the same as that of the recrystallized chloride.

Sulfanuryl chloride is readily soluble in benzene and ether. It crystallizes excellently from 85-95° petroleum ether (prepared from "overshoe" gasoline) or from benzene. It is also soluble in alcohol, but the solution turns acid at once - this probably involves the formation of an ester of sulfanuric acid. Sulfanuryl chloride reacts energetically with ammonia and with amines, both in aqueous solutions and in the absence of water. As its structural formula indicates, sulfanuryl chloride must exist as two geometrical isomers: cis with all three chlorine atoms on one side of the ring; and trans, with two chlorine atoms on one side of the ring and one on the other side. Inasmuch as the stereo structure of the α-substance is still unknown, it must be called α-sulfanuryl chloride.

The yield of the β-substance was about 18.5% of the theoretical. The elementary composition and molecular weight of the β-substance did not differ from those of the α-sulfanuryl chloride, it being a stereo isomer of the latter appar-

ently. Thus, the α- and β-substances are most likely two of the theoretically possible geometrical isomers of sulfanuryl chloride. Inasmuch as the stereo structure of the β-substance is still unknown, we must call it β-sulfanuryl chloride. The β-sulfanuryl chloride has a much lower melting point than the α isomer (145.5° for the α and 47.5° for the β) and is much more soluble in petroleum ether. For example, 1.0 g of the α compound dissolves in 100 g of petroleum ether (bp. 70-75°, from "overshoe" gasoline), while 1.0 g of the β compound dissolves in 2.5 g of the same petroleum ether at the same temperature. What is more, the β compound sublimes more easily than the α one. The β isomer deflagrates in the same way as the α isomer when heated on a platinum spatula or in a test tube. When we hydrolyzed β-sulfanuryl chloride in hot water, we noticed that some of the substance escaped with the vapor without decomposing and that hydrolysis involved an intermediate stage in which some high-melting substances were formed. β-Sulfuranyl chloride is hydrolyzed at a rate approximating that of the α compound.

The physical properties of the isomeric sulfanuryl chlorides led us to think that the α compound is the trans-sulfanuryl chloride, while the β compound is the cis-sulfanuryl chloride, but this question can be definitely settled only after a more thorough study of the physical and chemical properties of both compounds.

EXPERIMENTAL

Thermal cleavage of trichlorophosphaszosulfuryl chloride. 0.5 mol of trichlorophosphazosulfuryl chloride (125.44 g) with a m.p. of 33° was placed in a flask for vacuum distillation, fitted with a 300-mm herringbone dephlegmator, a capillary for supplying air, and a thermometer with its bulb immersed in the substance. The air that entered the capillary was first desiccated in a Tishchenko bottle containing calcium chloride. The receiver was chilled to -20° with a freezing mixture. The flask was heated over an oil bath, first to 130°, and toward the end to 150°. The pressure within the system was maintained at 8 mm during the reaction. The reaction set in when the temperature of the bath was 130° and that of the liquid was 113°; the temperature of the vapor was 22.5°. The temperature of the bath was raised to 145° in the course of 10-15 minutes, which caused the liquid's temperature to rise to 121-122° at first and then to drop to 118.5°, after which it began to rise again when 10 minutes had elapsed. Apparently, 118.5° is the decomposition temperature of the acid chloride. Twenty minutes after the onset of the reaction the driving off of the phosphorus oxychloride increased noticeably, the vapor temperature rising to 25°, and then beginning to drop gradually. The phosphorus oxychloride usually crystallized in the receiver. The reaction was complete within 70 to 80 minutes, the end of the reaction being easily noted by the temperature of the liquid rising to 129° (at a bath temperature of 150°) and by the temperature of the vapor dropping to 21.5° (at a room temperature of 19°). The phosphorus oxychloride entrained other high-boiling reaction products, which condensed in the column and thus were not collected in the distillate. The reaction balance was as follows: residue in the flask - 53.64 g, in the column - 0.49 g, total residue - 54.13 g; theoretical yield 48.76 g. The yield of phosphorus oxychloride with a m.p. of 0.6 g totaled 67.21 g, while the losses totaled 4.10 g. If the losses are due to the phosphorus oxychloride, the overall yield of phosphorus oxychloride was 71.31 g, or 92.98% of the theoretical. Thus, the reaction follows the reaction adopted, but there is no doubt that some 8% of the trichlorophosphazosulfuryl chloride decomposes without evolving the oxychloride.

The reaction product was a transparent, faintly brownish liquid, from which rather numerous colorless crystals settled out upon cooling. Large transparent prisms settled out at room temperature; cooling to -10° caused the further settling out of numerous acicular crystals. When the crystalline deposit was suction-filtered at room temperature, most of the product left on the filter was the high-melting α compound, which is slowly hydrolyzed by water. When the crystalline deposit was suction-filtered at 0°, three substances are left on the filter, namely: the α, then the low-melting, difficultly hydrolyzable β, and finally the γ, a readily hydrolyzable solid. The quantity of suction-filtered substance left on the filter is not diminished by mixing it thoroughly with ice water, hydrolysis being very slow; but when the temperature of the mixture is raised to 10°, the γ substance is quickly hydrolyzed, the temperature rising sharply to 40-60° (if not much water is present), and the β substance fusing and passing through the filter as an oil that crystallizes upon cooling, leaving the pure α substance upon the filter. This procedure involves the hydrolysis of appreciable quantities of α and β as well. It is better, therefore, to effect separation as follows. The reaction product was left to stand for a day at room temperature, after which the crystals that settled out, containing practically all the α substance, some of the β, and some of the readily hydrolyzable γ substances, were suction-filtered and pressed out. The yield of the crude α product totaled 17-19 g. The substance was thoroughly mixed with 75 ml of ice water to get rid of the readily hydrolyzable impurities, after which the mixture was heated to 15° for 10 minutes, the product being suction-filtered and washed four times with 10 ml of water heated to 15°. After suction-filtering, the substance was immediately desiccated in a 0.5-mm vacuum above sulfuric acid at room temperature. This yielded 13.12 g of a snow-white crystalline substance that consisted of the α product with a slight trace of β. To eliminate the latter the substance was washed four times with 5-ml batches of 85-95° petroleum ether, leaving a residue of 11.92 g, or about 24% of the theoretical quantity of the α substance, with a m.p. of 141-144°. The substance was recrystallized from ten times its weight of (85-95°) petroleum ether for final purification. The substance settled out as large prisms or platelets clustered into large aggregates, with an uncorrected m.p. of 144.5-145.5°. The losses in recrystallization were negligible. See the general section for the properties of this substance.

The filtrate left after recovery of α was distilled in a 7-mm vacuum. With an oil-bath temperature of 160°, a small quantity distilled at 120-125°, the bulk passing over at 125-129°, after which distillation came to a stop, the flask contents boiling up violently at a bath temperature of 196°, though this caused no rise in pressure and nothing was distilled. The flask residue (probably the γ substance plus its decomposition products) was cooled, turning into a thick, dark-brown mass, which was not investigated any further for the moment, while the distillate (18.85 g) was a transparent lemon-yellow liquid. As the distillate was cooled, large prisms of the β substance settled out. After being allowed to stand at room temperature for a day, the distillate was chilled to 5° during the course of two hours, and the crystalline deposit was suction-filtered out. The yield was 8.15 g. To remove the readily hydrolyzable impurities, the substance was treated with 30 ml of ice water, the mixture being heated to 15° for 10-15 minutes, and the substance suction-filtered, washed three times with 10-ml batches of water heated to 15°, and immediately desiccated above sulfuric acid at room temperature and a vacuum of 0.5 mm. The substance was successively treated on a suction filter with 10, 5, and 5-ml batches of 85-95° petroleum ether, in which the β substance

is readily soluble, to get rid of the traces of the α product. Driving off the petroleum ether in vacuum left 6.05 g of crude β-sulfanuryl chloride in the flask, as large, colorless prisms with a m.p. of 42.0-43.5°.

The filtrate left after isolating the β (about 10.5 g) contained considerable β and a low-melting, readily hydrolyzable, δ substance. The filtrate was agitated with 100 ml of water to eliminate the δ substance. Most of the substance was hydrolyzed within the course of a few minutes, the residue crystallizing rapidly. It was suction-filtered after standing for 30 minutes, washed, and desiccated. This yielded another 3.00 g of β substance with a m.p. of 41-42.5°. The total yield of the crude β-sulfanuryl chloride was about 9.0 g, or about 18.5% of the theoretical. To secure an absolutely pure substance, the crude product was dissolved in as little light petroleum ether as possible, the slight quantity of the insoluble α compound being filtered out, and three-quarters of the solvent being driven off in a slight vacuum at 30-35°. As the solution was chilled, the sulfanuryl chloride settled out as large transparent prisms, up to 5 mm long, with a m.p. of 46-47°. The recrystallized substance was finally purified by sublimation in a 5-mm vacuum at 80°. The sublimed β-sulfanuryl chloride consisted of minute lustrous transparent prisms with a m.p. of 47-47.5°. The melting point quickly fell to 42-43° when it was exposed to the air.

The δ substance has not been isolated in the pure state as yet, though its yield is rather high, approximately 7.5 g, or some 15.3% of the theoretical. It is not impossible that the δ substance is a mixture of several substances.

When the crude α or β substance was desiccated in vacuum desiccators, the vaseline on the inside of the ground-glass surfaces was turned into a dark-brown, malodorous mass – these substances apparently contained some volatile impurities that reacted with the vaseline. This phenomenon was not observed when the pure α and β substances were kept in vacuum desiccators.

When we washed out the herringbone dephlegmator with benzene after the reaction, we noticed that the benzene was colored a bright golden-yellow. Driving off the benzene in vacuum left behind a nearly colorless oily liquid, which colored benzene a bright golden-yellow again when dissolved in it. A much fainter color was observed when the crude decomposition product and the distillate containing the β and δ products were dissolved in benzene. The color disappeared instantly when a drop of water was added. The distilled phosphorus oxychloride did not produce this color with benzene.

The reaction products thus include a very small quantity of still another substance ε, it seems, which colors benzene a bright golden-yellow that vanishes when the benzene is driven off. The same color is produced by gasoline that contains unsaturated compounds. If there are no unsaturated compounds in the gasoline, the contents of the column dissolve in it without any coloration.

Analysis of α-sulfanuryl chloride. All the analyses were performed in the usual manner.

0.0496 g subs.: 0.0002 g H_2O; 0.0503 g subs.: 0.0002 g H_2O; 0.2048 g subs.: 8 50 ml 0.5 N alkali; 0.3014 g AgCl; 0.2212 g substance: 9.15 ml 0.5 N alkali; 0.3228 g AgCl; 0.1021 g subs.: 0.2437 g $BaSO_4$; 0.0928 g subs.: 0.2216 g $BaSO_4$. 0.1538 g substance: 15.65 ml 0.1 N acid; 0.1583 g substance: 16.15 ml 0.1 N acid; 0.3390 g substance; 16.16 g benzene: Δt 0.367°; 0.4397 g subs.: 16.16 g benzene: Δt 0.481°. Found %; H 0.04, 0.04; Cl 36.39, 36.08; S 32.78, 32.80; N 14.26, 14.29. Acid equivalent found upon hydrolysis: 6.072, 6.054. M 292.5, 289.6. $(NSOCl)_3$. Calculated %. H 0.00; Cl 36.35; S 32.87; N 14.39. Calculated acid equivalent upon hydrolysis 6.000; M 292.56.

Analysis of β-sulfanuryl chloride. All the analyses were performed in the usual manner.

0.0643 g substance: 0.0001 g H_2O; 0.0662 g substance: 0.0001 g H_2O; 0.1012 g subs. 0.1485 g AgCl; 0.1016 g subs. 0.1486 g AgCl. 0.0867 g subs. 0.2061 g $BaSO_4$; 0.0830 g substance: 0.1980 g $BaSO_4$; 0.2564 g substance: 26.30 ml 0.1 N acid; 0.2579 g substance: 26.55 ml 0.1 N acid; 0.2743 g substance: 11.20 ml 0.5 N alkali; 0.3213 g substance: 13.25 ml 0.5 N alkali; 0.1248 g substance; 15.51 g benzene: Δt 0.145°; 0.2517 g substance; 15.51 g benzene: Δt 0.288°. Found %: H 0.02, 0.02; Cl 36.31, 36.19; S 32.65, 32.76; N 14.37, 14.42. Acid equivalent found upon hydrolysis: 5.967, 6.027; M 285.2, 289.7. $(NSOCl)_3$. Calculated %: H 0.00; Cl 36.35; S 32.87; N 14.39. Calculated acid equivalent upon hydrolysis 6.000; M 292.56.

SUMMARY

It has been shown that the thermal cleavage of trichlorophosphazosulfuryl chloride results in the formation of phosphorus oxychloride and products of the transformation of sulfanyl chloride.

Two trimers of sulfanyl chloride have been isolated from these products, and it has been shown that these trimers are most likely two theoretically possible stereo isomers of sulfanuyrl chloride or 1,3,5-trichloroxo-1,3,5-trithiatriazine. The properties of the two isomeric sulfanuryl chlorides are described.

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Chair of Organic Chemistry,
The J. V. Stalin Metallurgical Institute of Dnepropetrovsk, Awarded the Order of the Red Banner of Labor.

See p. 101, this issue.

TRICHLOROPHOSPHAZOSULFURYL CHLORIDE

A. V. Kirsanov

Research on the reaction of sulfamic acid with phosphorus pentachloride is of considerable interest, inasmuch as we may hope to secure the hitherto unknown sulfamyl chloride in this reaction, or else some more highly complicated product related to sulfamyl chloride.

The reaction of sulfamic acid and phosphorus pentachloride has been investigated by F. Ephraim and M. Gurewitsch [1], who found that one molecule of sulfamic acid reacts with two molecules of phosphorus pentachloride, the second molecule of the phosphorus pentachloride decomposing (at 90-100°!) into chlorine and phosphorus trichloride, the latter combining with the sulfamyl chloride to form the stable binary compound $ClSO_2NH_2 \cdot PCl_3$.* Ephraim and Gurewitsch were unable to cleave this latter compound into its components. Inasmuch as Ephraim and Gurewitsch fail to supply adequately substantiated data in the experimental section of their paper in support of the composition and structure of the product of the reaction between sulfamic acid and phosphorous pentachloride, and inasmuch as there are weighty reasons [2] for not trusting the accuracy of Ephraim's and Gurewitsch's findings, we resolved to make our own study of the reaction of sulfamic acid and phosphorus pentachloride. This study indicated that most of the data reported by Ephraim and Gurewitsch were wrong and that the compound $ClSO_2NH_2 \cdot PCl_3$ either is nonexistent or has not been synthesized as yet, the compound to which Ephraim and Gurewitsch assigned this composition and structure being altogether different.

As our experiments have shown, finely pulverized sulfamic acid readily reacts with powdered phosphorus pentachloride at the temperature of a boiling water bath, exactly two molecules of phosphorus pentachloride reacting with one molecule of sulfamic acid. Three molecules of hydrogen chloride and one molecule of phosphorus oxychloride are evolved in the reaction. The overall reaction is therefore: $NH_2SO_2OH + 2PCl_5 \rightarrow 3HCl + POCl_3 + SO_2NPCl_4$. The reaction sets in faster and comes to an end faster when carbon tetrachloride is present.

Ephraim and Gurewitsch assert that chlorine is evolved during the reaction. That is true, chlorine actually being liberated, but in very minute quantities, viz: 0.35% of the theoretical, based on the reaction proposed by Ephraim and Gurewitsch. It should be added that this quantity of chlorine is very much less than that evolved when trichloroacetamide is reacted with phosphorus pentachloride or when pure phosphorus pentachloride is heated to 100-110° for approximately the same length of time [3]. Hence, the evolution of chlorine undoubtedly has no direct relation to the main reaction.

According to Ephraim and Gurewitsch, the reaction product left after the phosphorus oxychloride was removed consisted of "a thick, dark-brown liquid that did not crystallize at room temperature." This is untrue, the reaction product actually being a wholly transparent, colorless, rather mobile liquid, which crystallized quickly at room temperature and melted at 23° (maximum, with the thermometer bulb immersed in the liquid). Ephraim and Gurewitsch apparently used highly impure initial substances, which may also be the reason

*The reaction is as follows: $NH_2SO_2OH + 2PCl_5 \rightarrow HCl + POCl_3 + ClSO_2NH_2 \cdot PCl_3$.

for their asserting that phosphorus trichloride was formed in the reaction.

The composition of the reaction product leads us to think that its structure is that of $ClSO_2N{=}PCl_3$, i.e., it is trichlorophosphazosulfuryl chloride. This supposition is borne out by determination of its molecular wt., by the analytical findings - determination of hydrogen, sulfur, chlorine, and phosphorus - and by the fact that hydrolysis of the substance yields seven acid equivalents (with thymolphthalein) as follows:

$$ClSO_4N{=}PCl_3 \xrightarrow{+H_2O} 4HCl + HOSO_2ONH_4 + H_2HPO_4.$$

The assertion of Ephraim and Gurewitsch that phosphorus acid is produced by hydrolysis is incorrect, only phosphoric acid being formed.

The yield of the crude acid chloride, with a m.p. of 23°, was 99.45% of the theoretical, based on the sulfamic acid entering into the reaction, but this product contains a rather large percentage of some low-melting impurities, which can be readily eliminated by suction-filtering, evidently as a eutectic with the acid chloride. The acid chloride thus prepared consists of snow-white crystals with a m.p. of 33° (thermometer bulb in the liquid), the yield of the pure product being about 75% of the theoretical. The melting point was raised to 35-36° after several recrystallizations from petroleum ether, all moisture being excluded (thermometer bulb in the liquid). The composition of the products with melting points of 33° and 36° is the same, however, the crude acid chloride having nearly the same composition as the refined preparations. Hence, the "impurities" have the same composition as the acid chloride, and are either its polymers or isomers.

It should be stressed that the stated yields and composition of the reaction products are secured only when pure and absolutely dry sulfamic acid and pure phosphorus pentachloride are used (it is best to use freshly prepared phosphorus pentachloride and not more than 2.06 mols of the latter per mol of the sulfamic acid). When too great an excess of phosphorus pentachloride is employed, the yield of the solid product is diminished, the melting point of the crude acid chloride drops sharply, and the elementary composition of the crude product changes. When commercial products are used as the initial substances, there is a great difference between the composition of the crude acid chloride and the product suction-filtered after crystallization, while the yield of the pure acid chloride is reduced appreciably. These are probably the reasons for the inaccurate data secured by Ephraim and Gurewitsch.

Trichlorophosphazosulfuryl chloride is readily soluble in benzene, ether, and carbon tetrachloride and slightly soluble in petroleum ether, its solubility rising somewhat when the latter is hot. Trichlorophosphazosulfuryl chloride is extremely hygroscopic, deliquescing rapidly in the air. When the crude product, with a m.p. of 23°, is mixed with water at room temperature, it reacts violently, with a characteristic noise, within a few seconds. The suction-filtered acid chloride, with a m.p. of 33°, reacts somewhat more quietly with water, tiny particles rapidly "running" over the surface of the water. Hydrolysis is much slower at 0°. The reaction of the acid chloride with a concentrated aqueous solution of ammonia or with gaseous ammonia is very violent. The acid chloride reacts as readily with alcohols, amines, and phenols. The acid chloride underwent no change, at least in the course of 16 months, when kept in a sealed ampoule. The acid chloride may be distilled in vacuum, provided the quantity is not too large (up to 5 g) and distillation is rapid.

Its b.p. is 135-140° at 7 mm.

Even rapid distillation, however, is accompanied by partial decomposition, the melting point of the distilled product always being lower than that of the initial substance. When 5 g of the acid chloride with a m.p. of 33° was distilled, for instance, we secured 4.0 g of acid chloride with a m.p. of 21°.

When the acid chloride is distilled slowly, it undergoes a highly interesting decomposition, which has been reported in the previous paper (p. 93.).

The high chemical activity of trichlorophosphazosulfuryl chloride and its availability are grounds for expecting that this acid chloride may serve as the starting point for the synthesis of diversified derivatives of sulfamic and phosphazosulfuric acids.

EXPERIMENTAL

Experiments using 0.05 to 0.1 mol of sulfamic acid were performed in order to make a quantitative determination of all the products of the reaction between sulfamic acid and phosphorus pentachloride. In the preparative synthesis of trichlorophosphazosulfuryl chloride we used up to 2 mols of sulfamic acid. Typical experiments of both types are described below.

Reaction of sulfamic acid with phosphorus pentachloride. 0.1 mol (9.71 g) of thoroughly pulverized anhydrous sulfamic acid and 0.2 mol (41.65 g) of freshly prepared phosphorus pentachloride were placed in a 100-ml round-bottomed flask. The phosphorus pentachloride was weighed out and charged into the flask in a dry chamber. The flask was closed with an inclined reflux condenser, filled with brine at a temperature of -17°. The outlet end of the condenser was connected to three absorbing vessels in series, with tubes reaching to above the surface of the liquid. The first absorber was filled with 300 ml of a 1.0N solution of alkali, the second and third each containing 100 ml of the 1.0N solution of alkali. The absorbers were chilled with ice water. The flask containing the reaction mixture was immersed in a boiling water bath. The evolution of hydrogen chloride set in at once, as was evident from the "current" in the liquid within the first absorber. Phosphorus oxychloride, entrained by the current of hydrogen chloride, soon began to condense within the reflux condenser, a small amount of sublimed phosphorus pentachloride depositing on the inner tube of the condenser. (Should the phosphorus pentachloride be deposited on the neck of the flask, an attempt must be made to wash it off with the refluxed oxychloride, turning the flask to get at all the deposit, or else the flask must be plunged more deeply into the bath.) The reaction mixture began to liquefy within an hour, becoming wholly liquid after two hours, and the reaction came to an end after two hours and a half had elapsed. The reaction product was a colorless, transparent, mobile liquid containing a small quantity of minute crystals. It was qualitatively determined in a special test that these were crystals of unreacted sulfuric acid. The weight of the reaction products totaled 38.33 g, i.e., including the escaping hydrogen chloride, phosphorus oxychloride, phosphorus pentachloride, and 13.03 g of chlorine. The phosphorus oxychloride was driven off over a water bath with an "isolated" vacuum and a receiver that was chilled to -20°. The distillate consisted of 13.4 g of phosphorus oxychloride with a m.p. of 0.8°, the m.p. of a fusion sample being likewise 0.8° (thermometer bulb in the liquid). The residue weighed 24.43 g, indicating that the loss of phosphorus oxychloride during evacuation was 0.05 g and making the total yield of phosphorus oxychloride 13.9 g, or 90.61% of the theoretical, not allowing for

any that escaped with the hydrogen chloride during the reaction. The residue in the flask was suction-filtered through a tiny weighed filter fitted with a porous glass plate in order to recover the sulfamic acid, which was washed with anhydrous benzene. The sulfamic acid recovered weighed 0.32 g, or 3.30% of the quantity charged into the flask. In the titration of this sulfamic acid we used 3.4 ml of a 1.0N alkali solution, equivalent to 0.33 g, or 3.40% of the quantity charged into the flask. Hence, the yield of the crude trichlorophosphazosulfuryl chloride was 24.11 g, or 96.12% of the theoretically possible, or 99.45% based on the reacted sulfamic acid. The recovery of the pure product and its properties are described below, under the preparative method used for synthesizing the acid chloride.

The phosphorus pentachloride deposited within the condenser was quickly removed with a special spatula and weighed, after which the condenser was washed with 250.0 ml of water to which 50.0 ml of a 1.0N alkali solution had been added. The phosphorus pentachloride scraped off the condenser was cautiously added to this solution, and the excess alkali was titrated back with a 1.0N acid solution containing thymolphthalein. The phosphorus pentachloride recovered weighed 0.62 g, or 1.49% of the amount placed in reaction, while 0.69 g, or 1.66% of the quantity placed in the reaction, was found by titration (26.76 ml of a 1.0N alkali solution, i.e., 23.24 ml of 1.0N alkali solution was required to neutralize the phosphoric and hydrochloric acids).

The contents of all three absorbers were transferred quantitatively to a 1-liter flask, and the contents of the latter were brought up to 1000 g. 500 g of this solution was used to titrate the active chlorine with a 0.1 N solution of hyposulfite, 3.52 ml of the latter being consumed, which was the equivalent of 0.0125 g of free chlorine. Hence a total of 0.0250 g of free chlorine was evolved during the reaction, or 0.175% of the theoretical quantity, based on the phosphorus pentachloride, that is, much less than the percentage that Wallach found was evolved [3] when phosphorus pentachloride was reacted with trichloroacetamide or when pure phosphorus pentachloride was heated to 100-110° for about the same length of time. If we go by the Ephraim and Gurewitsch equation, the free chlorine evolved totaled 0.35% of the theoretical quantity.

The other half of the solution was used to determine the acidity, but first 100-g batches of the solution were boiled for 2-3 hours with reflux condensers to decompose the hypochlorous acid. 16.20 ml of a 1.0N acid solution containing thymolphthalein was required per 100 g of the solution. Therefore the solution contained 0.338 equivalent of acid or, allowing for the hydrogen chloride remaining within the apparatus (derived volume of about 120 ml), 0.343 equivalent. Of this total 0.0276 equivalent must have resulted from the phosphorus oxychloride entrained by the hydrogen chloride (as computed from the difference between the theoretical yields of the acid chloride and the yield of the phosphorus oxychloride, which totaled 5.51%), while 0.0319 equivalent must have resulted from the phosphorus pentachloride entrained by the hydrogen chloride (based on the difference between 100% and the overall yield of the acid chloride and the per cent of phosphorus pentachloride found in the condenser, which totaled 2.28%). Thus, 0.283 equivalent of hydrogen chloride was formed in the main reaction (ignoring the percentage of free chlorine because of its minuteness), or 97.59% based on the reacted sulfamic acid.

Reaction balance sheet. 0.1 mol of sulfamic acid was used, of which 0.9665 mol entered into the reaction; 0.2 mol of phosphorus pentachloride

was used. The yield of the crude acid chloride was 96.12% of the theoretical. The yield of the crude acid chloride was 99.45% based on the reacted sulfamic acid. The yield of phosphorus oxychloride totaled 0.9061 mol. The acids formed when the gaseous reaction products reacted with water totaled 0.343 equivalent. 0.060 equivalent of acids must have been formed from the phosphorus oxychloride and pentachloride entrained with the hydrogen chloride. The hydrogen chloride evolved during the main reaction totaled 0.283 equivalent. The hydrogen chloride evolved was 97.59%, based on the reacted sulfamic acid. The free chlorine evolved totaled 0.35% of the theoretical, based on the Ephraim and Gurewitsch equation.

These figures definitely prove that the principal reaction involved in the interaction of sulfamic acid with phosphorus pentachloride follows the equation given above.

Preparative synthesis of trichlorophosphazosulfuryl chloride. 2 mols (184.2 g) of sulfamic acid, dried at 100° in vacuum and pulverized, and 4.12 mols (858 g) of pulverized phosphorus pentachloride were placed in a 2-liter round-bottomed flask fitted with a reflux condenser. 100 ml of anhydrous carbon tetrachloride was added to the mixture, and the flask was held down in a boiling water bath. The evolution of hydrogen chloride set in soon. Within 30 minutes the reaction mixture began to liquefy noticeably, turning into a transparent colorless liquid within two hours. An appreciable quantity of phosphorus pentachloride was deposited within the condenser. The reaction ended after two and a half hours had elapsed, and after the reaction mixture had cooled, it was suction-filtered to remove the minute quantity of unreacted sulfamic acid (about 0.5 g).

The phosphorus oxychloride and the carbon tetrachloride were driven off in vacuum, over a boiling water bath toward the end of the process. In one of the tests, run without adding any carbon tetrachloride, we secured 284 g, or 92.5% of the theoretical, of phosphorus oxychloride with a m.p. of +0.8°. The residue left after the phosphorus oxychloride had been driven off – the crude trichlorophosphazosulfuryl chloride – was a nearly colorless, transparent liquid that rapidly crystallized when chilled into a dense radiating mass of crystals saturated with liquid. The yield of the crude product was 497.7 g, or 99.2% of the theoretical based on the sulfamic acid. The preparation fused readily, the last crystal vanishing at 23° (thermometer bulb in the liquid).

The next day the product was suction-filtered and thoroughly pressed out. This yielded 325 g, or 65% of the theoretical, of trichlorophosphazosulfuryl chloride as a snow-white crystalline mass with a m.p. of 33° (maximum, with the thermometer bulb in the liquid; supercooling to 29°). The filtrate was chilled to -10°, a seed crystal was added, and the whole was suction-filtered one hour later. This yielded 51 g, or about 10% of the theoretical, of the acid chloride with a m.p. of 32°. The total yield of solid product with a m.p. of about 33° was 376 g, or 75% of the theoretical. A little more of the solid acid chloride could be secured by even deeper chilling of the filtrate, which was a nearly colorless oily liquid.

All the operations involved in suction-filtering the acid chloride should be performed in a dry cabinet or in a well-ventilated laboratory on extremely cold days. The acid chloride decomposes very slowly in air when the outside temperature is below -20° and there is a draft in the laboratory. The acid chloride may also be suction-filtered and pressed out "under rubber", but

then the top layer of the substance is darkened by contact with the rubber.

The acid chloride was recrystallized (in a dry cabinet) from petroleum ether that had a b.p. of 75-85°, prepared from "overshoe" gasoline, all of whose unsaturated compounds had been eliminated by repeated treatment with sulfuric acid. The trichlorophosphazosulfuryl chloride crystallized from the petroleum ether as colorless needles with a m.p. of 35-36°. It is best to keep the acid chloride in the molten state, as the product is decomposed much more rapidly by atmospheric moisture when the container is opened or when it is taken from the desiccator, if it is in the shape of individual crystals.

Analyses of trichlorophosphazosulfuryl chloride. One of the decisive factors in proving that the products of the interaction of phosphorus pentachloride and sulfamic acid had the structure of trichlorophosphazosulfuryl chloride is the presence or absence of hydrogen in it. The hydrogen was determined by the usual combustion method.*

It is quite obvious that this percentage of hydrogen can only be due to the accidental entrace of atmospheric moisture, so that the structure suggested for the substance by Ephraim and Gurewitsch is indisputably wrong.

The phosphorus, the sulfur, the chlorine, and the acid equivalent produced during hydrolysis were determined by the customary methods after a sample of the substance had been hydrolyzed by an excess of 0.5N solution of sodium hydroxide. The nitrogen was determined after a sample of the substance had been hydrolyzed in water, followed by hydrolysis in concentrated hydrochloric acid. The molecular weight was determined cryoscopically in benzene. In the subjoined analyses for P, S, and Cl, the first two figures refer to the crude acid chloride, the third and fourth to the preparation with a m.p. of 32-33°, and the fifth and sixth to the preparation with a m.p. of 35-36°. In the molecular weight determinations the first two figures refer to the preparation with a m.p. of 32-33°, and the third and fourth to the preparation with a m.p. of 35-36°.

0.3513 g, 0.3625 g, 0.4002 g, 0.3091 g, 0.3416 g and 0.3523 g substance: 0.1565 g, 0.1620 g, 0.1771 g, 0.1367 g, 0.1508 g and 0.1558 g $Mg_2P_2O_7$. 0.2709 g, 0.2485 g, 0.2520 g, 0.2170 g, 0.2361 g and 0.2219 g substance: 0.2508 g, 0.2304 g, 0.2342 g, 0.2016 g, 0.2192 g and 0.2062 g $BaSO_4$. 0.1429 g, 0.1381 g, 0.1545 g, 0.1420 g, 0.1388 g and 0.1325 g substance: 0.3240 g, 0.3136 g, 0.3516 g, 0.3237 g, 0.3162 g and 0.3017 g AgCl. 0.2610 g, 0.2653 g, 0.2574 g, 0.2645 g, 0.2549 g and 0.2674 g substance: 10.25 ml, 10.45 ml, 10.20 ml, 10.50 ml, 10.10 ml, 10.60 ml 0.1 N acid. 0.3774 g, 0.3796 g, 0.3663 g, 0.3667 g, 0.3895 g and 0.3897 g substance: 10.65 ml, 10.70 ml, 10.25 ml, 10.25 ml, 10.90 ml and 10.90 ml 1.0 N alkali. 0.0986 g, 0.1593 g, 0.1156 g and 0.1828 g substance. 18.0 g benzene: Δt 0.112°, 0.184°, 0.132° and 0.211°. Found %: P 12.41, 12.46, 12.33, 12.32, 12.29, and 12.32; S 12.72, 12.73, 12.76, 12.76, 12.75 and 12.76; Cl 56.08, 56.15, 56.33, 56.37, 56.33 and 56.32; N 5.50, 5.52, 5.55, 5.56, 5.55 and 5.55. Found: acid equiv. in hydrolysis: 7.08, 7.07, 7.02, 7.01, 7.02 and 7.02; M 247.4, 244.2, 247.5 and 243.8.

$ClSO_2NPCl_3$. Calculated %: P 12.37; S 12.78; Cl 56.54; N 5.59. Calculated: acid equivalent in hydrolysis 7.00. M 250.92.

SUMMARY

It has been shown that a satisfactory yield of trichlorophosphazosulfuryl chloride is produced by reacting phosphorus pentachloride with sulfamic acid.

*0.1232 g subs.: 0.18 mg H_2O; 0.1103 g subs.: 0.24 mg H_2O. Found %: H0.016, 0.024.

It has been shown that the findings by Ephraim and Gurewitsch to the effect that the reaction of sulfamic acid with phosphorus pentachloride yields a binary compound of phosphorus trichloride and sulfamyl chloride are incorrect, and that all data concerning that compound should be deleted from textbooks and the reference literature.

The properties and the method of preparation of trichlorophosphazosulfuryl chloride are described.

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THE REACTIVITY OF ORGANIC HYDROXIDES OF MERCURY

THE REACTION OF PHENYLMERCURY HYDROXIDE WITH PHENOLS

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Dimroth [1] has shown that phenols are mercurated very easily, yielding ortho and para substitution products. The reaction is such that almost always we obtain dimercurated, and sometimes trimercurated, phenols, into addition to the monomercurated one. M. M. Koton and T. M. Zorina [2] have shown that when diphenylmercury and dinaphthylmercury are reacted with phenols, monomercurated, dimercurated, and trimercurated derivatives of the phenols are produced. Koton and Chernov [3] have found that similar products are formed when tolyl derivatives of mercury are reacted with the phenols. Koton [4] made a study of the reaction of mercury derivatives of the C_6H_5HgAc and also secured monomercurated, dimercurated, and trimercurated phenol derivatives.

It is known that hydroxides of organometallic compounds are highly reactive, so that the reaction of organic hydroxides of mercury with the phenols must be of considerable interest.

The present paper is a study of the reaction of phenylmercury hydroxide with the following phenols: p-nitrophenol, o-nitrophenol, 2,4-dinitrophenol, trinitrophenol, p-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, resorcinol, and pyrogallol. The reaction was carried out at 130° with and without solvents present. As might have been expected, the experiments in which alcohol was used resulted in the evolution of metallic mercury.

In our study of the reaction of phenylmercury hydroxide with phenols we have found that phenols may be readily mercurated by introducing an ArHg radical, using phenylmercury hydroxide; dimercurated phenol derivatives constituted the bulk of the reaction products, with trimercurated derivatives occurring in some instances. When the reaction conditions were milder (100°), monomercurated compounds were produced. It should be stressed that mercuration via C_6H_5HgOH is easier than with $(C_6H_5)_2Hg$ and its functional derivatives; this inference follows from the fact that under identical conditions $(C_6H_5)_2Hg$ yields mono- and dimercurated derivatives, while C_6H_5HgOH yields nothing but dimercurated derivatives.

EXPERIMENTAL

All our experiments on the reaction of phenylmercury hydroxide with the phenols were made by heating a mixture of the substances to 130° in sealed glass ampoules.

1. Phenylmercury hydroxide and p-nitrophenol. 0.3 g of p-nitrophenol was used for 0.3 g of phenylmercury hydroxide. Heating lasted 3 hours. Two principal products were recovered from the (yellow) reaction mixture by successively treating it with aqueous alcohol, alcohol, and benzene. The excess

p-nitrophenol (0.21 g) was recovered from the aqueous alcohol solution. The principal reaction product was a heavy, yellow, infusible powder (0.2640 g) that was insoluble in organic solvents.

0.05 g substance: 2.86 ml 0.1 N. NH_4CNS. Found %: Hg 57.20. $(C_6H_5Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 57.96.

This compound is therefore the dimercurated derivative of p-nitrophenol.

2. Phenylmercury hydroxide and o-nitrophenol. The experimental conditions and the subsequent processing of the reaction mixture were the same as in the case of the p-nitrophenol. The aqueous alcoholic solution yielded 0.268 g of the yellow crystals of the unreacted o-nitrophenol, with a m.p. of 41-42°. The alcohol yielded 0.1148 g of the colorless crystals of the unreacted hydroxide.

The residue consisted of 0.1618 g of a heavy yellow powder that was infusible up to 300°, which was purified and then analyzed for mercury.

0.05 g substance: 2.82 ml 0.1 N. NH_4CNS. Found %: Hg 56.23. $(C_6H_5Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 57.96.

Hence, this compound is the dimercurated derivative of o-nitrophenol.

3. Phenylmercury hydroxide and 2,4-nitrophenol. The experimental conditions and the subsequent processing of the reaction mixture were the same as in the case of the p-nitrophenol.

A total of 0.1328 g of crystals with a m.p. of 109-111° was recovered from the aqueous alcoholic solution. This represented the excess 2,4-dinitrophenol. A total of 0.1014 g of yellowish crystals with a m.p. of 126-127° was recovered from the alcoholic solution. This was a mixture of the excess 2,4-dinitrophenol and phenylmercury hydroxide. The residue was the yellow-orange powder of the dimercurated derivative, which was insoluble and infusible up to 250°. The impurities were eliminated from the compound by dissolving it in alkali and precipitating it with CO_2.

0.05 g substance: 2.72 ml 0.1 N NH_4CNS. Found %: Hg 54.40. $(C_6H_5Hg)_2C_6H(OH)(NO_2)_2$. Calculated %: Hg 54.50.

As we see from the analysis, this compound is the dimercurated derivative of 2,4-dinitrophenol.

4. Phenylmercury hydroxide and 2,4-dinitrophenol. This experiment was run at 100°, the processing of the reaction mixture being the same as that for the p-nitrophenol.

A total of 0.221 g of crystals with a m.p. of 111-112° – the excess 2,4-dinitrophenol – was recovered from the aqueous alcohol. A total of 0.2108 g of the yellow crystals of the monomercurated derivative of 2,4-dinitrophenol was recovered from the alcohol.

0.05 g substance: 2.123 ml 0.1 N NH_4CNS. Found %: Hg 42.46 $C_6H_5GgC_6H_2(OH)(NO_2)_2$. Calculated %: Hg 43.69.

The residue contained 0.0135 g of an insoluble and infusible, pale-yellow powder – the dimercurated derivative.

0.0135 g substance: 0.70 ml 0.1 N NH_4CNS. Found %: Hg 54.23. $(C_6H_5Hg)_2C_6H(OH)(NO_2)_2$. Calculated %: Hg 54.50.

5. Phenylmercury hydroxide and 2,4-dinitrophenol. This experiment was

run with alcohol present, the reaction mixture being processed as in the case of the p-nitrophenol.

5.1% of free mercury was found. 0.1100 g of an insoluble and infusible dark-brown powder was recovered.

0.05 g substance: 2.66 ml 0.1 N NH_4CNS. Found %: Hg 53.20.
$(C_6H_5Hg)_2C_6H(OH)(NO_2)_2$. Computed %: Hg 54.50.

Hence, this compound is the dimercurated derivative of 2,4-dinitrophenol.

6. Phenylmercury hydroxide and trinitrophenol. The experimental conditions and the processing of the reaction mixture were the same as those used for the p-nitrophenol.

A total of 0.2119 g of yellow crystals with a m.p. of 98° - apparently the unreacted picric acid with a trace of the phenylmercury hydroxide - was recovered from the aqueous alcoholic solution. The alcoholic solution yielded 0.2925 g of a nearly colourless powder with a m.p. of 158°.

0.05 g substance: 1.96 ml 0.1 N NH_4CNS. Found %: Hg. 39.20.
$C_6H_5HgC_6H(OH)(NO_2)_3$. Computed %: Hg 39.60.

Hence, this compound is the monomercurated derivative of picric acid.

7. Phenylmercury hydroxide and p-chlorophenol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

In this experiment 6.53% of free mercury was evolved. 0.1868 g of an infusible product that was insoluble in organic solvents was obtained.

0.05 g substance: 11.608 ml 0.05 N $Na_2S_2O_3$. Found %: Hg 58.04.
$(C_6H_5Hg)_2C_6H_2(OH)Cl$. Computed %: Hg 58.23.

The analytical data indicate that this insoluble powder was the dimercurated derivative of p-chlorophenol.

8. Phenylmercury hydroxide and 2,4-dichlorophenol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

A total of 0.1486 g of the excess 2,4-dichlorophenol, with a m.p. of 47°, was recovered from the aqueous alcoholic solution. The insoluble and infusible product totaled 0.1904 g.

0.05 g substance: 11.056 ml 0.05 N $Na_2S_2O_3$. Found %: Hg 55.28
$)C_6H_5Hg)_2C_6H(OH)Cl_2$. Computed %: Hg 55.94.

The analysis indicates that this was the dimercurated derivative of 2,4-dichlorophenol.

9. Phenylmercury hydroxide and 2,4,6-trichlorophenol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

0.1 g of the trichlorophenol, with a m.p. of 79°, was recovered from the aqueous alcoholic solution. A total of 0.141 g of crystals with a m.p. of 86° - apparently a mixture of the trichlorophenol and the phenylmercury hydroxide - was recovered from the alcoholic solution. The residue, which was insoluble and fused at 300° (with decomposition) and totaled 0.2102 g, was the dimercurated derivative of 2,4,6-trichlorophenol.

0.05 g substance: 10.584 ml 0.05 N $Na_2S_2O_3$. Found %: Hg 52.92.
$(C_6H_5Hg)_2C_6H(OH)Cl_2$. Computed %: Hg 53.30.

10. Phenylmercury hydroxide and resorcinol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

Brown crystals with a m.p. of 107° – the excess resorcinol – were recovered from the aqueous alcoholic solution. The residue was 0.2320 g of a dark-red infusible substance.

0.05 g substance: 3.19 ml 0.1 N NH_4CNS. Found %: Hg 63.80 $(C_6H_5Hg)_3C_6H(OH)_2$. Calculated %: Hg 64.03.

Hence, the insoluble residue was the trimercurated derivative of resorcinol.

11. Phenylmercury hydroxide and pyrogallol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

A total of 28.34% of free mercury was evolved.

12. Phenylmercury hydroxide and pyrogallol. This experiment was performed in ethyl alcohol.

A total of 41.43% of free mercury was evolved in the experiment.

SUMMARY

1. It has been established, for the first time, that phenylmercury hydroxide is able to mercurate the phenols.

2. The principal reaction products in the mercuration of the phenols were the dimercurated derivatives.

3. It has been shown that phenylmercury hydroxide is more highly reactive than other organomercury compounds in the mercuration of phenols.

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**See C.B. English translation, p. 709.

THE REACTION OF ORTHODITOLYLMERCURY WITH ORGANIC ACIDS

I. A. Chernov

It has been shown in an earlier paper [1] that para and orthoditolylmercury react with organic acids, forming acyl derivatives of the $CH_3C_6H_4HgOCOR$ type. It was found that orthoditolylmercury is highly reactive. Only the reactions of orthoditolylmercury with some acids (formic, acetic, isovaleric, lactic, oxalic, and salicylic acids) have been explored. We were interested in making a more thorough study of these reactions with various organic acids.

Further study was undertaken of the reactions of orthoditolylmercury with the following monobasic saturated acids: butyric, myristic, palmitic, and stearic acids, as well as with the following halogen substitution derivatives of monobasic saturated acids: chloroacetic, bromoacetic, and trichloroacetic acids. Of the monobasic acids, the reactions of orthoditolylmercury with the following acids were investigated: succinic, glutaric, adipic, azelaic, maleic, fumaric, and tricarballylic acids. Of the aliphatic hydroxy acids, tartaric and citric acids were tested, and of the aromatic acids, benzoic, gallic, sulfosalicylic and phthalic acids.

Orthoditolylmercury generally reacts with acids as follows: $(CH_3C_6H_4)_2Hg + RCOOH \longrightarrow CH_3C_6H_5 + RCOOHgC_6H_4CH_3$. The resulting acyl derivatives were isolated in the pure state, and the conditions governing their formation, their melting points, and their solubility in various solvents were established. The acyl derivatives of saturated monobasic acids are white crystalline substances with low melting points (below 90°) that are freely soluble in organic solvents.

It should be noted that orthoditolylmercury reacts very readily (at room temperature) with the halogen substitution derivatives of monobasic saturated acids, yielding crystalline compounds of the following general formula: $CH_2HalCOOHgC_6H_4CH_3$. Tracing the reactions of orthoditolylmercury with dibasic acids is likewise of interest. Succinic acid, for example, yields disubstituted acyl derivative of the $CH_3C_6H_4HgOCO(CH_2)_2COOHgC_6H_4CH_3$ type, whereas the following representatives of the homologous series: glutaric, adipic, and azelaic acids, as less reactive even under more severe conditions (100°, heating for 3 hours), yield nothing but monosubstituted derivatives of the $CH_3C_6H_4HgOCO(CH_2)_nCOOH$ type. Reactions with maleic and fumaric acids are no less interesting. Maleic acid, which is a cis isomer, reacts more energetically with orthoditolylmercury, forming a disubstituted product, whereas fumaric acid yields only a monosubstituted product.

Tartaric acid, which is a hydroxy derivative of succinic acid, also yields a disubstituted acyl derivative. Citric acid behaves differently, yielding a monosubstituted derivative. Orthoditolylmercury reacts normally with aromatic acids: monobasic benzoic and gallic acids, yield monobasic acyl

derivatives, while sulfosalicylic and phthalic acids yield disubstituted derivatives.

EXPERIMENTAL

All the tests were run under the conditions set forth above [1]. The mercury content was determined in the usual manner, the Whitmore and Sobatzki method [2] being used only for the halogen-substitution acids.

Orthoditolylmercury and n-butyric acid. 0.2 g of orthoditolylmercury and 1 ml of butyric acid were reacted together at room temperature for 96 hours. As the aqueous solution cooled, a white precipitate settled out that was soluble in ether, alcohol, acetone and benzene, and dissolved when heated in water. The m.p. of orthotolylmercury butyrate is 86-87°. The yield was 0.125 g (63.1% of the theoretical).

0.03 g substance: 1.569 ml 0.1 N NH_4CNS. Found %: Hg 52.30. $C_{11}H_{14}O_2Hg$. Calculated %: Hg 53.00.

Orthoditolylmercury and myristic acid. 0.2 g of orthoditolylmercury and 0.14 g of myristic acid were heated together for 3 hours to 100°. The white waxlike deposit was heated gently with alcohol, after which aqueous alcohol was added and the precipitate was filtered out. Recrystallization from acetone yielded a white powder that was soluble in ether and benzene, soluble when gently heated in alcohol and acetone, and insoluble in water. The m.p. of orthotolylmercury myristate is 71°. The yield was 0.1 g (37% of the theoretical).

0.03 g substance: 1.151 ml 0.1 N NH_4CNS. Found %: Hg 38.37. $C_{21}H_{34}O_2Hg$. Calculated %: Hg 38.68.

Orthoditolylmercury and palmitic acid. 0.2 g of orthoditolylmercury and 0.15 g of palmitic acid were heated to 100° for 3 hours. The resulting light-brown hyaline mass was treated with warm alcohol, after which aqueous alcohol was added and the resultant precipitate was filtered out. Recrystallization from alcohol yielded a white powder that was soluble in ether, acetone, and benzene, soluble when heated in alcohol and insoluble in water. The m.p. of orthotolylmercury palmitate is 69-70°. The yield was 0.14 g (49% of the theoretical).

0.05 g substance: 1.82 ml 0.1 N NH_4CNS. Found %: Hg 36.40. $C_{23}H_{38}O_2Hg$. Calculated %: Hg 36.70.

Orthoditolylmercury and stearic acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of stearic acid for 3 hours. The resulting greenish-brown mass was treated with warm alcohol, the resulting solution being poured into a beaker, where it solidified into a dense mass. After the latter had been recrystallized from aqueous alcohol, the precipitate was filtered out and desiccated. The resulting light-brown powder was soluble in ether and benzene, soluble when heated in alcohol and acetone, and insoluble in water. The m.p. of orthotolylmercury stearate is 59°. The yield was 0.18 g (59% of the theoretical).

0.03 g substance: 1.026 ml 0.1 N NH_4CNS. Found %: Hg 34.20. $C_{25}H_{42}O_2Hg$. Calculated %: Hg 34.31.

Orthoditolylmercury and chloroacetic acid. Reacting 0.2 g of orthoditolylmercury with 0.1 g chloroacetic acid for 96 hours at room temperature yielded a grayish-white precipitate. The later was dissolved in water, the solution being poured out into cold water. The faintly colored resulting precipitate was filtered out and dessicated. The precipitate was soluble in ether, alcohol, acetone, and benzene, and (when heated) in water. The m.p. of orthotolyl-

mercury chloroacetate is 81°. The yield was 0.16 g (80% of the theoretical).

0.1 g substance: 10.50 ml 0.05 N $Na_2S_2O_3$. Found %: Hg 52.47. $C_9H_9O_2ClHg$. Calculated %: Hg 52.09.

Orthoditolylmercury and bromoacetic acid. 0.2 g of orthoditolylmercury was reacted with 0.1 g of bromoacetic acid for 96 hours at room temperature, resulting in the formation of a white precipitate. The latter was treated with water, the solution being poured out into water. The precipitate that settled out was soluble in ether, acetone, and benzene, and (when heated) in alcohol and water. The m.p. of orthotolylmercury bromoacetate is 82-83°. Its yield was 0.19 g (84.8% of the theoretical).

0.1 g substance: 9.50 ml 0.05 N $Na_2S_2O_3$. Found %: Hg 47.52. $C_9H_9O_2BrHg$. Calculated %: Hg 46.69.

Orthoditolylmercury and trichloroacetic acid. 0.2 g of orthoditolylmercury was reacted with 0.1 g of trichloroacetic acid for 96 hours at room temperature, resulting in the formation of a brown powder. The latter was treated with water, the solution being poured out into cold water. Filtration and desiccation yielded a white powder that was soluble in ether, benzene, and acetone, and (when gently heated) in alcohol, but was only slightly soluble in water. The m.p. of orthotolylmercury trichloroacetate is 112-114°. Its yield was 0.19 g (80.2% of the theoretical).

0.1 g substance: 9.02 ml 0.05 N $Na_2S_2O_3$. Found %: Hg 45.08. $C_9H_7O_2Cl_3Hg$. Calculated %: Hg 44.18.

Orthoditolylmercury and succinic acid. 0.2 g of orthoditolylmercury was heated with 0.07 g of succinic acid in the presence of one drop of water to 100° for 1 hour. The resultant white precipitate was heated in alcohol, the flask contents then being poured out into cold water. The precipitate thrown down was filtered out, desiccated, and heated with acetone. The precipitate was insoluble in water or in the following organic solvents: ether, alcohol, acetone, or benzene. The m.p. of orthoditolylmercury succinate is 200° with decomposition. The yield was 0.06 g (16.4% of the theoretical).

0.02 g substance: 1.15 ml 0.1 N NH_4CNS. Found %: Hg 57.53. $C_{18}H_{18}O_4Hg_2$. Calculated %: Hg 57.38.

Orthoditolylmercury and glutaric acid. 0.2 g of orthoditolylmercury was heated with 0.08 g of glutaric acid in the presence of one drop of water to 100° for 3 hours. The resultant light-brown precipitate was heated in water, the flask contents then being transferred to cold water. The resulting precipitate was filtered out and then recrystallized from acetone. The m.p. of orthotolyl glutarate is 105-106°. The yield was 0.04 g (17.5% of the theoretical). The substance was insoluble in ether or water, but soluble in acetone and (when heated) in alcohol and benzene.

0.02 g substance: 0.942 ml 0.1 N NH_4CNS. Found %: Hg 47.10. $C_{12}H_{14}O_4Hg$. Calculated %: Hg 47.46.

Orthoditolylmercury and adipic acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of adipic acid in the presence of one drop of water to 100° for 3 hours. The fused product was treated with hot water and filtered out. A precipitate of orthotolylmercury adipate, with a m.p. of 94-96°, settled out of the solution. The yield was 0.15 g (65.9% of the theoretical). The precipitate was insoluble in water or ether, though soluble when heated in alcohol, acetone, and benzene.

0.05 g substance: 2.332 ml 0.1 N NH_4CNS. Found %: Hg 46.64. $C_{13}H_{18}O_4Hg$. Calculated %: Hg 45.95.

Orthoditolylmercury and azelaic acid. 0.2 g of orthoditolylmercury was heated with 0.12 g of azelaic acid in the presence of one drop of water to 100° for 3 hours. The fused resulting light-brown mass was gently heated with aqueous alcohol and filtered out, yielding a light-brown product that dissolved when heated in water, alcohol, acetone, and benzene, and was insoluble in ether. Orthotolylmercury azelate has a m.p. of 85-87°. Its yield was 0.16 g (64% of the theoretical).

0.05 g substance: 2.061 ml 0.1 N NH_4CNS. Found %: Hg 41.22. $C_{16}H_{22}O_4Hg$. Calculated %: Hg 41.91.

Orthoditolylmercury and maleic acid. 0.2 g of orthoditolylmercury and 0.08 g of maleic acid were heated together with one drop of water for 3 hours at 100°. The fused resulting light-brown mass was gently heated in aqueous alcohol and filtered out yielding a white precipitate that was insoluble in water or these organic solvents: either, alcohol, acetone, and benzene. The m.p. of orthoditolylmercury maleate is 186-188° with decomposition. The yield was 0.15 g (41.2% of the theoretical).

0.05 g substance: 2.856 ml 0.1 N NH_4CNS. Found %: Hg 57.11. $C_{18}H_{16}O_4Hg_2$. Calculated %: Hg 57.54.

Orthoditolylmercury and fumaric acid. 0.2 g of orthoditolylmercury was heated with 0.08 g of fumaric acid and one drop of water to 100° for 3 hours. The fused resulting light-brown mass was heated gently in aqueous alcohol. Filtration yielded a light-pink product that was insoluble in water or in these organic solvents: ether, alcohol, acetone, and benzene. The m.p. of orthotolylmercury fumarate is 184-185° with decomposition. The yield was 0.17 g (80% of the theoretical).

0.05 g substance: 2.447 ml 0.1 N NH_4CNS. Found %: Hg 48.95. $C_{11}H_{10}O_4Hg$. Calculated %: Hg 49.33

Orthoditolylmercury and tricarballyic acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of tricarballylic acid and one drop of water to 100° for 3 hours. The dark precipitate was treated with cold water and filtered out. Treatment with hot alcohol yielded a light-brown precipitate that was insoluble in water, ether, alcohol, acetone, or benzene. The m.p. of orthotolylmercury tricarballylate is 199-200° with decomposition. The yield was 0.08 g (32.8% of the theoretical).

0.3 g substance: 1.276 ml 0.1 N NH_4CNS. Found %: Hg 42.54. $C_{13}H_{14}O_8Hg$. Calculated %: Hg 42.99.

Orthoditolylmercury and tartaric acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of tartaric acid and one drop of water to 100° for 1 hour. The resultant white precipitate was treated with cold water and filtered out. Subsequent processing with hot water yielded a white substance that was insoluble in ether, alcohol, acetone, benzene, or water. The m.p. of orthoditolylmercury tartrate is 191° with decomposition. The yield was 0.16 g (40% of the theoretical).

0.03 g substance: 1.621 ml 0.1 N NH_4CNS. Found %: Hg 54.04. $C_{18}H_{18}O_8Hg_2$. Calculated %: Hg 54.87.

Orthoditolylmercury and citric acid. 0.2 g of orthoditolylmercury was heated with 0.2 g of citric acid and one drop of water to 100° for 3 hours.

The resulting gray precipitate was treated with cold water and filtered out. This yielded a white precipitate that was insoluble in water or in the following organic solvents: ether, alcohol, acetone, and benzene. The m.p. of orthotolylmercury citrate is 150-152° with effervescence. The yield was 0.12 g (52.2% of the theoretical).

0.05 g substance: 2.29 ml 0.1 N NH_4CNS. Found %: Hg 45.80. $C_{18}H_{14}O_7Hg$. Calculated %: Hg 45.63.

Orthoditolylmercury and benzoic acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of benzoic acid to 100° for 1 hour. The resulting gray precipitate was treated with cold water and filtered out. The resulting tacky mass crystallized after some time had elapsed, turning into a white powder that was soluble in organic solvents. The m.p. of orthotolylmercury benzoate is 58-60°. The yield was 0.1 g (46.3% of the theoretical).

0.05 g substance: 2.395 ml 0.1 N NH_4CNS. Found %: Hg 47.90. $C_{14}H_{12}O_2Hg$. Calculated %: Hg 48.61.

Orthoditolylmercury and gallic acid. 0.2 g of orthoditolylmercury was heated with 0.12 g gallic acid and one drop of water to 100° for 1 hour. The resulting gray powder was gently heated with water and filtered out. This yielded a gray powder that was soluble when heated in alcohol and in acetone and was insoluble in water, ether, or benzene. The m.p. of orthotolylmercury gallate is 133° with decomposition. Its yield was 0.17 g (70.5% of the theoretical).

0.05 g substance: 2.155 ml 0.1 N NH_4CNS. Found %: Hg 43.10. $C_{14}H_{12}O_5Hg$. Calculated %: Hg 43.55.

Orthoditolylmercury and sulfosalicylic acid. 0.2 g of orthoditolylmercury was heated to 100° for 1 hour with 0.15 g of sulfosalicylic acid and one drop of water. The fused resultant light-brown mass was treated with cold water and filtered out, yielding light-brown rhombic crystals that were soluble in ether, acetone, and benzene, and (when heated) in water and in alcohol. The m.p. of orthoditolylmercury sulfolsalicylate is 101-102°. Its yield was 0.17 g (40.7% of the theoretical).

0.03 g substance: 2.531 ml 0.1 N NH_4CNS. Found %: Hg 50.62. $C_{21}H_{18}O_6SHg_2$. Calculated %: Hg 50.20.

Orthoditolylmercury and phthalic acid. 0.2 g of ditolylmercury was heated to 100° for 1 hour with 0.1 g of phthalic acid and one drop of water. The fused resulting light-brown mass was treated with alcohol and filtered out, after which it was retreated with hot alcohol. This yielded a lustrous white powder that was soluble when heated in alcohol or benzene and was insoluble in water or ether. The m.p. of orthoditolylmercury phthalate is 174-175°. The yield was 0.15 g (38.5% of the theoretical).

0.03 g substance: 1.59 ml 0.1 N NH_4CNS. Found %: Hg 53.00. $C_{22}H_{18}O_4Hg_2$. Calculated %: Hg 53.69.

SUMMARY

1. A study has been made of the reactions of orthoditolylmercury with various organic acids.

2. It has been shown that these reactions yield acyl derivatives of the general formulas $CH_3C_6H_4HgOCOR$ and $CH_3C_6H_4HgOCORCOOHgC_6H_4CH_3$ which are crystalline substances with definite melting points, most of which are soluble

in organic solvents.

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*See C.B. English translation, p. 345.

POLYMERIZATION – DEPOLYMERIZATION

VII. THE STRUCTURE OF THE TETRAMER OF ISOBUTYLENE

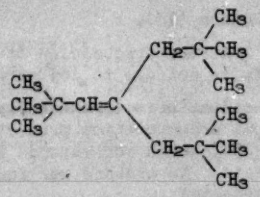
Ya. M. Slobodin and E. M. Markova

The polymerization of isobutylene with sulfuric acid was investigated long ago by Butlerov [1], who secured the dimer and trimer forms. Isobutylenes of higher molecular weight were prepared by Lebedev [2], who polymerized butylene with silicates. It was found that the mean molecular weight of the polymers depended upon the polymerization temperature (Lebedev and Borgman [3]) as well as upon the nature of the silicates (Slobodin [4]).

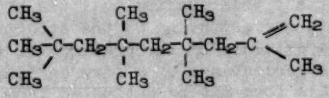
The polymerization of isobutylene may be represented satisfactorily enough by Whitmore's diagram, in which a carbon ion is formed as an intermediate product [5]. Among the dimers and trimers of isobutylene forms have been found that were predicted by this diagram and are in full agreement with it.

The structure of the tetraisobutylenes has been unknown up to the present time. Using Whitmore's diagram to explain their formation, we might expect the three isomeric tetraisobutylenes represented below to be formed, with the first form predominating (Petrov [6]):

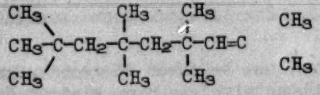
(I)



(II)



(III)



We employed ozonolysis to investigate the structure of the tetramers of isobutylene in the present research, besides studying their Raman spectra. The chemical and physical research methods yield identical results. The Raman spectra were also photographed in the laboratory of the Institute of Physics of the University of Leningrad (headed by Prof. E. F. Gross).

It was found that the spectra of the tetrameric forms of isobutylene contain two double-bond frequencies, 1637 and 1650 cm^{-1}, after they had been separated from the other polymeric forms.

The tetramer was separated in vacuo into two fractions with b.p. of 89° at 3 mm and 92-94° at the same pressure. The spectra of these fractions each contained two double-bond frequencies: 1634 and 1652 cm^{-1} in the spectrum of the first tetramer, and 1629 and 1645 cm^{-1} in the spectrum of the second.

These findings indicate that the tetramer of isobutylene is a mixture of at least two isomeric forms with the same kind of double bond.

There is no doubt that vacuum fractionation without an efficient enough separatory column cannot separate the mixture into the individual hydrocarbons. The difference between the spectra of these fractions indicates that one isomer predominates in one fraction, and the other isomer in the other.

The Raman spectra are convincing proof that neither of these two fractions contains any appreciable percentages of hydrocarbons that are symmetrical disubstituted or trisubstituted ethylenes, since these latter hydrocarbons all possess a double-bond frequency of the order of 1670 cm^{-1}. All the isomeric tetramers of isobutylene in these fractions must contain the

group.

This group is covered by Structure (II).

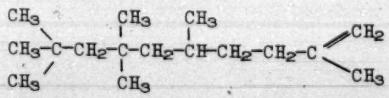
It should also be noted that the frequencies of 1629 and 1634 cm^{-1} are too low. A check proved that this is not due to any error of measurement.

Both of the tetramer fractions were then ozonolyzed, the following compounds being found to be the principal decomposition products in each case: a ketone with the molecular weight of 230, which corresponds to the empirical formula $C_{15}H_{30}O$ ($\underline{M}$=226), and formic acid. No acetone was found, but a small quantity of trimethylacetic acid was detected.

The results of ozonolysis thus confirm that the bulk of the isobutylene tetramer consists of a form corresponding to the structure (II). The presence of trimethylacetic acid is evidence of the presence in the tetramer of spectrographically indeterminable percentages of a form corresponding to the structure (I). The percentage of this form may be estimated from our data as approximately 10%. The same quantitative ratio follows from a comparison of the yields of the trimethylacetic acid. The tetramer forms have no isomer corresponding to the structure (III).

As we have stated above, the tetramer of isobutylene is a mixture of at least two isomeric hydrocarbons with the same kind of double bond. Judging by the intensity of the frequencies, we may assume that the percentages of these isomers are about the same. Though the above findings clearly indicate the structure of one of these isomers, various surmises may be ventured as to the structure of the others. Another isomer may be the addition product of a molecule of isobutylene and its trimer on the "end-to-end" principle, which would correspond to the structure (IV):

(IV)



A different distribution of the methyl groups in the tetramer is not impossible, as indicated by the research of Petrov [7] on the destructive hydrogenation of polyisobutylenes under pressure. At the present time, we do not rule out the possibility that these and other forms are present.

Still, the adoption of any of the foregoing structures for the second tetramer of isobutylene does not explain the reason for the appreciable drop in the frequency of the double bond. We incline to relate this phenomenon to the presence of "rotational isomerism" [8].

It should be said that examination of the Raman spectra indicates the presence of a similar phenomenon for the pentamers and still higher polymers of isobutylene. We have made a study of these problems in conjunction with Prof. E. F. Gross and published them in a separate report [8].

EXPERIMENTAL

The tetramer of isobutylene was prepared by polymerizing isobutylene above floridin, chilling with ice water being used. Vacuum fractionation yielded a fraction with a b.p. of 107-112° at 17 mm.

The tetramer was then separated into fractions with a b.p. of 87-89° at 3 mm, 92-94° at 3 mm, and 102-105° at 3 mm, though only the first two fractions were analyzed.

Fraction with a b.p. of 87-89° (3 mm). d_4^{20} 0.7932; n_D^{20} 1.44807; γ^{20} 26.44 dynes/cm. Found: $\underline{MR}_D$ 75.53; P 644; M 229. $C_{16}H_{32}$. Calculated: $\underline{MR}_D$ 75.62; P 647; M 224.

Raman spectrum (frequencies in cm^{-1}): 210(5), 533(3), 573(1), 688(4W) 724(10), 747(8), 772(4), 825(4), 874(3), 937(1), 990(1), 1005(3), 1034(4), **1115(3)***, 1177(2), 1205(5), 1253(4), 1290(3), 1323(3), 1402(4), **1407**(8) 1453(5), 1471(3), **1634**(6), **1652(6)**, 2490(1), 2779(8), 2904(3), 3074(4).

Fraction with a b.p. of 92-94° (3 mm). d_4^{20} 0.7938; n_D^{20} 1.44927; γ^{20} 24.99 dynes/cm. Found: $\underline{MR}_D$ 75.53; P 631; M 222. $C_{16}H_{32}$. Calculated: $\underline{MR}_D$ 75.62; P 647; M 224.

Raman spectrum (frequencies in cm^{-1}): 243(2), 310(1), 462(2), 553(1), 557(3), 583(3), 588(2), 618(2), 628(3), 678(4 W), 722(8), 744(10), 767(4), 821(4), 869(3), 889(4 W), 976(1), 1029(3), 1067(4), **1113**(3), 1167(2), 1199(5), 1204(4), 1276(3), 1314(3), **1403(4 W)**, 1444(10), 1467(5), **1629(3)**, 1645(10W), 2490(1), 2528(8), 2779(3), 2977(4), **3080(4)**.

Ozonolysis of the tetramer. Both fractions were ozonated. We cite the results of only one test, inasmuch as practically identical results were secured with both fractions.

We used 8.8 g of the substance and 20 ml of anhydrous chloroform in ozonation. The ozone was passed through at the rate of 15 liters per hour at -70°. When saturation with ozone was complete, the chloroform was driven off at a low vacuum. The ozonide was decomposed by boiling it with water, decomposition being extremely slow. There were two layers in the flask after the reaction was over. The upper oily layer was separated, vacuum-distilled, and analyzed. The yield was 5.6 g.

0.1410 g substance: 0.4133 g CO_2; 0.1651 g H_2O. Found %: C 79.93; H 13.01; M 230. $C_{15}H_{30}O$. Calculated %: C 79.65; H 13.27; M 226.

*Here and subsequently, bold face numbers relate to the group $-C\begin{matrix}=CH_2\\ \diagdown CH_3\end{matrix}$.

The bottom, aqueous layer was neutralized with potash until its reaction was faintly alkaline, and the neutral products were extracted with ether. A test for acetone with 2,4-dinitrophenylhydrazine was negative. Driving off the ether left 0.2 g of the substance, which was treated with freshly-prepared silver oxide. The reaction products were diluted with water and thoroughly boiled, and the excess silver oxide was filtered out. Evaporating the filtrate yielded only a small quantity of a formate, all of which decomposed when evaporated.

The alkaline solution, which contained salts of organic acids, was acidulated with dilute sulfuric acid. The formic acid was determined in a separate test by the calomel method. Recalculated for the total solution, the formic acid was found to total 1.17 g, which agrees with the amount of the ketone $C_{15}H_{30}O$ formed. The acidulated solution was extracted with ether, the ether solution being desiccated with calcium chloride. After the ether had been driven off, the acid residue was kept in a vacuum desiccator above a solid alkali to eliminate the formic acid. An acid with a m.p. of 28-32° crystallized out, this being the m.p. of trimethylacetic acid. A total of 0.18 g of the crystalline acid was collected, the silver salt being prepared from this total without purifying it. Found % Ag: 53.33%. $C_5H_9O_2Ag$. Calculated %: Ag 51.67. The excessive percentage of silver in the salt is due to incomplete elimination of the formic acid.

SUMMARY

1. It has been shown that the principal constitutent of the tetramer of isobutylene is 2,4,4,6,6,8,8-heptamethylnonene-1. Isomers with other arrangements of the methyl groups may also be present.

2. It has been found that only minor quantities of 2,2,6,6-tetramethyl-4-neopentylheptene-3, which ought to be the major constitutent of the tetramer of isobutylene according to Whitmore's diagram, are actually formed. Its percentage in the reaction product may be estimated at about 10%.

3. We have not found the third tetramer of isobutylene called for by Whitmore's diagram - 2,4,4,6,6,8,8-heptamethylnonene-2.

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POLYMERIZATION - DEPOLYMERIZATION

VIII. THE ACTION OF METALLIC SODIUM ON 1,4-DIBROMOBUTENE-2

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The present paper reports on a study of the products formed by the action of metallic sodium on 1,4-dibromobutene-2.

Dehalogenation may be imagined to occur in accordance with the following equations:

$$\text{(I)}\quad 2BrCH_2{-}CH{=}CH{-}CH_2Br \xrightarrow{Na} \begin{matrix} Br{-}CH_2{-}CH{=}CH{-}CH_2 \\ \quad\quad\quad\quad\quad\quad\quad\quad | \\ Br{-}CH_2{-}CH{=}CH{-}CH_2 \end{matrix}$$

$$\text{(II)}\quad 2BrCH_2{-}CH{=}CH{-}CH_2Br \xrightarrow{Na} \begin{matrix} CH_2{-}CH{=}CH{-}CH_2 \\ \quad | \quad\quad\quad | \\ CH_2{-}CH{=}CH{-}CH_2 \end{matrix}$$

The 1,8-dibromoctadiene-2,6 formed in Equation (I) may in turn react with sodium, yielding cyclic and aliphatic products:

$$\text{(III)}\quad \begin{matrix} CH_2{-}CH{=}CH{-}CH_2Br \\ | \\ CH_2{-}CH{=}CH{-}CH_2Br \end{matrix} \xrightarrow{Na} \begin{matrix} CH_2{-}CH{=}CH{-}CH_2 \\ | \quad\quad\quad | \\ CH_2{-}CH{=}CH{-}CH_2 \end{matrix}$$

$$\text{(IV)}\quad \begin{matrix} CH_2{-}CH{=}CH{-}CH_2{-}Br \\ | \\ CH_2{-}CH{=}CH{-}CH_2{-}Br \end{matrix} \xrightarrow{Na} [-CH_2{-}CH{=}CH{-}CH_2CH_2{-}CH{=}CH{-}CH_2]_x$$

The end product of the reaction ought to be cyclooctadiene in Equations (II) and (III). Reaction (IV) should lead to the formation of a high-molecular linear polymer of butadiene, in which all the butadiene molecules are linked together at their 1 and 4 carbon atoms. As we know, a polymer form of this kind cannot be produced by straight polymerization.

Turning to the probability that the products set forth above are formed and bearing in mind the structural chemical relationships and the strain existing in the end products, we must assume that it is hardly possible for cyclooctadiene to be formed in Equation (II), owing to the high order of the reaction.

It seemed that the dibromide formed in Equation (I) could react via either Equation (III) or Equation (IV) when dehalogenated further. We know, however, that the formation of ring systems is a rather complicated process. The facts known at the present time often contradict the strain theory. Thus a three-membered ring, which possesses the maximum strain, is formed more easily than other ring systems. It is harder for the less-strained four-membered ring to be formed. It is often impossible to produce rings with many members by dehalogenating dihalogen derivatives.

In the 1,8-dibromooctadiene-2,6 we investigated, ring-closure ought to convert it into a cyclooctadiene free from strain, but the great length of the chain and the presence of two double bonds make the probability of the end carbon atoms coming close together after the two bromo atoms have been split off extremely small, so that the eight-membered ring cannot be closed [1].

Study of the products of the debromination of 1,4-dibromobutene-2 by metallic sodium in anhydrous ether indicated that only aliphatic hydrocarbons in which the number of carbon atoms is a multiple of four are formed. We recovered hydrocarbons with eight and twelve carbon atoms. High-molecular polymer forms were also found. Splitting off the bromine is accompanied by redistribution of the hydrogen. The dimer and trimer forms are proton acceptors, so that they are transformed into octadiene and dodecatriene, respectively. The high-molecular form is thought to be a proton donor, so that it should exhibit an increased unsaturation.

Hydrogenating the dimer form by the Lebedev method [2] indicated that the substance adds two molecules of hydrogen, the first one being added very much faster than the other. The break in the hydrogenation curve is located at about 50% added hydrogen. Normal octane is formed as the result of hydrogenation.

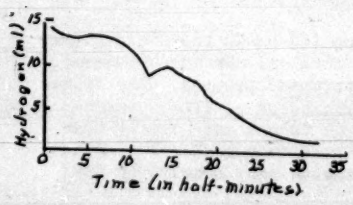
The molecular refraction of octadiene does not display any exaltation, which is evidence that no system of conjugated double bonds is present. This is also borne out by the inability of the hydrocarbon to react with maleic anhydride.

The Raman spectrum of octadiene exhibits two double-bond frequencies: 1635 and 1654 cm^{-1}, of identical intensity. The presence of two frequencies is proof that the double bonds are unequal. The presence of the 1415 and 3080 cm^{-1} frequencies in the spectrum leads us to believe that our octadiene contains the $CH_2=CH-$ group. This agrees with the double-bond frequency of 1635 cm^{-1}, which can refer only to this group in our compound.

The frequency of 1451 cm^{-1} and the presence of the frequencies of 997, 1370, and 2854 cm^{-1} in the spectrum indicate that the octadiene contains a methyl group, which agrees with the double-bond frequency of 1654 cm^{-1}, corresponding to the group $CH_3-CH=CH-$.

The foregoing indicates that the resulting octadiene has the structure of $CH_2=CH-CH_2-CH_2-CH_2-CH=CH-CH_3$.

Returning to the hydrogenation of this hydrocarbon, we may add that the course of the hydrogenation curve is like that of the hydrogenation curves of mixtures of mono- and symmetrical di-substituted ethylenes, which were exhaustively studied by Lebedev [3] (see drawing).



Thus, the dehalogenation of 1,8-dibromooctadiene-2,6 involves an allyl rearrangement only at one end of the chain. The reason for this may be that polarization results in the establishment of changes of opposite sign at the ends of the eight-carbon-atom complex produced by debromination. One part of these complexes is a proton acceptor and is converted into octadiene, while the other part

is a proton donor, so that it becomes more highly unsaturated and is readily polymerized to high-molecular products.

A similar state of affairs prevails in the trimer fraction, which has the empirical formula of $C_{12}H_{18}$ and contains three double bonds.

EXPERIMENTAL

1,4-Dibromobutene-2 was prepared from technical butadiene by the Thiele method [4]. The m.p. of the bromide was 52-53° after freezing and crystallization.

A solution of the bromide in absolute ether was placed in a large vessel and metallic sodium in the shape of 0.5 mm-diameter wire was added in several batches. About 1.5 liters of the ether were used for 500 g of the bromide. To make sure that the solution always contained a fresh sodium surface, small batches were added daily until the total sodium exceeded the calculated quantity by 10-15%. In some instances the addition of the initial portions caused the mixture to heat up. After the vessel had cooled down, it was allowed to stand at room temperature. The end of the reaction was indicated by the solution failing to give a positive Beilstein test for halogen. The reaction lasted from one to three months, depending upon the quantity of bromide used. As a rule, the solution turned brownish by the end of the reaction. We noticed that increasing the concentration of the bromide slowed the reaction down, while sunlight accelerated it. A total of 3000 g of the bromide was processed. After the reaction was over the ether solution was separated from the precipitate, and the ether was driven off. The residual oil was distilled at a low vacuum in a current of carbon dioxide. The residue consisted of a brownish, vaselinelike polymer. The distilled fraction had a b.p. of 60-65° at 80 mm.

The yield of the low-boiling hydrocarbon did not exceed 10%. The crude hydrocarbon was distilled over metallic sodium, the following fractions being collected:

1) 52-115° - 7.9%; 2) 115-128° - 15.4%; 3) 123-126° - 43.5%; 4) 126-132° - 14.0%; 5) 132-220° - 16.9%; and 6) losses and residue - 2.3%.

The hydrocarbon with a b.p. of 123-126° was the major constituent of the debromination products.

d_4^{20} 0.7576; n_D^{20} 1.43542; γ^{20} 22.92 dynes/cm. Found: MR_D 37.91; P 318; M 110. $C_8H_{14}F_2$. Calc. MR_D 38.21; P 324; M 100.

Raman spectrum (frequencies in cm^{-1}): 238 (1), 378 (1), 471 (1), 526 (1), 571 (1), 634 (1), 753 (1), 801 (1), 839 (2), 866(2), 919(2), 963(2), 997(2),1041(2), 1068 (2), 1081 (2), 1113 (1), 1149 (2), 1185 (2), 1215 (1), 1254 (8W), 1292 (8W), 1370 (3), 1415 (4), 1443 (7), 1451 (8), 1635 (10), 1654 (10W), 2854 (3), 2918 (8), 3015 (3), 3080 (3).

Bromine number by the McIlliney method, recomputed in terms of mols: 325, 320, 321. $C_8H_{14}F_2$. Calc. 320.

Lebedev hydrogenation. Adams platinic oxide [5] was employed as the catalyst. After the platinic oxide had been reduced, the hydrocarbon was placed in a "duck." The hydrogen consumption was read off every 0.5 minutes. The hydrocarbon weighed 0.6238 g.

Hydrogen consumption readings, ml (at 750.2 mm and 18.5°): 14; 13.1; 13.1; 13; 13; 12.9; 12.9; 12.6; 12.2; 11.4; 11; ‡‡ 8.8; 9.2; 9.9; 9.4; 9.1; 8.6; 8; 6.4; 6; 5.8; 4.8; 4.8; 3.8; 2.7; 2.6; 2.5; 2; 2; 2; 2; 1; 2; 1; 2.4; 2.2; 2.4; 2; 1.6; 1.4; 1; 1.2; 2.8; 0.6; 0.4; 0.6; 0.8; 0.1; 0.1; 0.1; 0.1.

The hydrogen consumption totaled 271 ml, or 250 ml at standard conditions. Calculations indicate that octadiene requires 254 ml. The symbol ‡ denotes the break in the hydrogenation curve. 139 ml of hydrogen, or 51.3%, were consumed up to the break.

13.7 g of the hydrocarbon were thoroughly hydrogenated to identify the hydrogenation product. After all the hydrogen had been added, the reaction mixture was poured into water, the hydrocarbon being separated, dried, and distilled. Its properties (b.p. 123-124°; d_4^{20} 0.7190; n_D^{20} 1.4034) were those of normal octane (b.p. 125.6°). The isomeric octanes boil within the 109-117° range.

Fraction with b.p. of 132-220°. Repeated fractionation yielded a hydrocarbon with a b.p. of 120-125° at 50 mm.

d_4^{20} 0.8244; n_D^{20} 1.45347; γ^{20} 24.72 dynes/cm. Found: MR_D 53.15; P 438; M 156 (cryoscopy in benzene). $C_{12}H_{18}F_3$. Calc. MR_D 54.07;* P 435; M 162.

Bromine number, recomputed in mols: 450; calc. for three double bonds: 480.

SUMMARY

1. Debromination of 1,4-dibromobutene-2 by metallic sodium in anhydrous ether splits off bromine, yielding 1,8-dibromoctadiene-2,6, which is then converted into octadiene-1,6, dodecatriene, and higher-molecular forms.

2. The reaction is an involved one. The high-polymer forms must exhibit increased unsaturation.

3. No cyclic hydrocarbons with four or eight carbon atoms are formed when bromine is split off from 1,4-dibromobutene-2, which agrees with the strain theory.

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*On the basis of $C_{12}H_{18}$ and four double bonds we get MR_D (exper.) = 52.50; and MR_D (calc.) = 53.55.

XV. REACTIONS BETWEEN THE SODIUM AND MAGNESIUM SALTS OF DIALKYL PHOSPHOROUS ACIDS AND ISOMERIC BUTOXYCHLOROPENTENES

A. N. Pudovik

In one of our previous papers [1] we made a study of the reactions between isomeric methoxychloropentenes and the sodium salts of dialkyl phosphorous acids. It was shown that the reactions are normal, without rearrangement, when the primary methoxychloropentene is employed, the reactions with secondary methoxychloropentenes differing, depending upon whether free dialkyl phosphorous acids are present in the reaction medium. When the acids are present alkoxy dialkyl phosphopentenes are formed, the structure of which is the same as that prepared from the primary methoxychloropentene; when they are absent, products of further addition of the sodium dialkyl phosphite being formed. Inasmuch as these reactions are of considerable theoretical interest, we resolved to pursue their study, using other compounds.

The present paper describes the reactions of the sodium and magnesium salts of dialkyl phosphorous acids with isomeric butoxychloropentenes. The reaction of 1-butoxy-5-chloropentene-3 with sodium diethyl phosphite in an excess of diethylphosphorous acid yielded 78.5% of 1-butoxy-5-diethylphosphopentene-3.

$$C_4H_9OCH_2CH_2CH{=}CHCH_2Cl + NaOP(OC_2H_5)_2 \longrightarrow$$
$$\longrightarrow C_4H_9OCH_2CH_2CH{=}CHCH_2PO(OC_2H_5)_2 + NaCl.$$

An analogous reaction with sodium dibutyl phosphite was unsuccessful, notwithstanding a wide variation in the reaction conditions employed, a hyaline mass that decomposed when heated in vacuo being produced in every instance. The reaction of 1-butoxy-3-chloropentene-4 with sodium diethylphosphite in benzene, with diethylphosphorous acid present, yielded 54% of 1-butoxy-5-diethylphosphopentene-3. Similarly, the reaction with sodium dibutylphosphite yielded 49% of 1-butoxy-5-dibutylphosphopentene-3.

Our experiments lead to the conclusion that the reactions of the Na salts of dialkyl phosphorous acids with 1-butoxy-3-chloropentene-4, like those with 1-methoxy-3-chloropentene-4, are monomolecular, involving a complete allyl rearrangement. When there are no free acids in the reaction medium, the reactions of 1-butoxy-3-chloropentene-4 with the sodium salts of dialkyl phosphorous acids result in the formation of thick, tacky products that cannot be distilled in vacuo.

Inasmuch as some of the reactions I carried out between salts of dialkyl

phosphorous acids and the isomeric butoxychloropentenes did not yield positive results, I endeavored to perform them with the corresponding magnesium salts. There are no definite statements in the literature regarding the feasibility of employing the magnesium salts of dialkyl phosphorous acids to synthesize phosphinic esters, so that a study of these reactions was of some theoretical interest.

The magnesium salts of the dialkyl phosphorous acids were initially prepared by adding a dialkyl phosphorous acid to an ether solution of ethylmagnesium bromide. We found that only about one third of the dialkyl phosphorous acid reacted, however, liberating ethane; adding the other two thirds of the acid had no effect. The reason for this peculiar trend of the reaction may be that the reaction of the diethylphosphorous acid with the Grignard reagent does not stop at the stage in which the magnesium salt of the diethylphosphorous acid is formed, but continues, yielding a salt of the dialkylphosphorous acid,

$$(C_2H_5O)_2P(=O)(MgBr) + 2C_2H_5MgBr \rightarrow (C_2H_5)_2P(=O)(MgBr) + 2C_2H_5OMgBr,$$

so that all the ethylmagesium bromide is rapidly removed from the reaction zone. Subsequently, the method used to prepare the magnesium salts of dialkyl phosphorous acids was modified so as add the Grignard reagent, prepared in ether, to a solution of the dialkyl phosphorous acid in benzene.

The action of magnesium diethylphosphite upon 1-methoxy-5-chloropentene-3 and 1-butoxy-5-chloropentene-3 yielded 1-methoxy-5-diethylphosphopentene-3 and 1-butoxy-5-diethylphosphopentene-3, the yields being 15.6 and 13.4%, respectively.

$$C_2H_5MgBr + HOP(OR)_2 \rightarrow (RO)_2P(=O)(BrMg) + C_2H_6$$

$$CH_3OCH_2CH_2CH{=}CHCH_2Cl + O(BrMg)P(OR)_2 \rightarrow$$

$$\rightarrow CH_3OCH_2CH_2CH{=}CHCH_2PO(OR)_2 + MgBrCl$$

The reaction of the mixed magnesium salt of diethylphosphorous acid with 1-methoxy-3-chloropentene-4 yielded 1-methoxy-5-diethylphosphopentene-3, the yield being 18.4%. We did not manage to secure the expected products when we reacted 1-butoxy-3-chloropentene-4 with the magnesium salts of diethyl or dibutylphosphorous acids, further heating of the reaction mixtures, after the solvent had been driven off, converting them into solid hyaline polymers.

We may infer from these experiments that the magnesium salts of dialkyl phosphorous acids may be successfully employed in some cases to synthesize phosphine esters instead of salts of the alkali metals, though the product yields are considerably lower. As when sodium salts are used, the reactions with the magnesium salts of dialkyl phosphorous acids are bimolecular, with no rearrangement, when the primary allyl halogen isomers are used, and monomolecular, with a complete allyl rearrangement, when the secondary isomers are used.

EXPERIMENTAL

Action of 1-butoxy-5-chloropentene-3 on sodium diethylphosphite. An ether solution of sodium diethylphosphite was prepared from 2 g of sodium and 12 g of diethylphosphorous acid, dissolved in 150 ml of absolute ether. 15 g of 1-butoxy-

5-chloropentene-3 was added gradually to the resultant solution, and then the mixture was heated on a water bath for 3 hours. A large quantity of sodium chloride was thrown down as soon as heating started. The sodium chloride was filtered out and washed repeatedly with ether, the ether being driven off and the residue distilled in vacuo. This yielded about 2 g of the original chloride, 1.5 g of a fraction that boiled in the 103-110° range (9 mm), and 19 g of 1-butoxy-5-diethylphosphopentene-3.

B.p. 169-171° (9 mm); n_D^{20} 1.4462; d_4^{20} 0.9918. 0.1384 g substance: 15.4 ml NaOH (T = 0.02085). Found %: P 10.84; $C_{13}H_{27}O_4P$. Calc. %: P 11.1.

Action of 1-butoxy-5-chloropentene-3 on dibutylphosphorous acid. 3.8 g of sodium was added to 28 g of dibutylphosphorous acid dissolved in 100 ml of anhydrous ether, and 26 g of 1-butoxy-5-chloropentene-3 was added after the sodium had dissolved. The reaction mass was heated on a water bath for 3 hours, the sodium chloride being filtered out and washed with ether. The ether was driven off, and the low-boiling fractions of the residue were distilled in vacuo. After it had been heated for a short time, it thickened into a transparent hyaline mass that decomposed when heated further.

Nor did repeated experiments, using a benzene solution and with an excess of dibutylphosphorous acid present, yield any positive results.

Action of 1-butoxy-3-chloropentene-4 on sodium diethylphosphite. 50 ml of absolute benzene and 30.7 g of 1-butoxy-3-chloropentene-4 were added to an ether solution of sodium diethylphosphite, prepared from 4 g of sodium and 48 g of diethylphosphorous acid. Sodium chloride began to precipitate out after the ether and part of the benzene had been driven off. The reaction mixture was heated on a water bath for 3 hours. The sodium chloride was filtered out and washed with ether. The ether and the benzene were driven off from the residue, the latter being fractionated in vacuo from a flask with a Widmer column. This yielded 5 g of the original chloride, 14 g of diethylphosphorous acid, and 26 g of 1-butoxy-5-diethylphosphopentene-3, whose constants were as follows: b.p. 169-171° (9 mm); n_D^{20} 1.4461; d_4^{20} 0.9918.

Action of 1-butoxy-3-chloropentene-4 on sodium dibutylphosphite. An ether solution of sodium dibutylphosphite was prepared from 40 g of dibutylphosphorous acid, 2.3 g of sodium, and 100 ml of anhydrous ether. 35 ml of anhydrous benzene and 18 g of 1-butoxy-3-chloropentene-4 were gradually added to the foregoing solution of sodium dibutylphosphite. The ether was driven off, and the reaction mass heated on a water bath for 3 hours. The sodium chloride was filtered out, and the reaction mass fractionated, yielding 16.5 g of 1-butoxy-5-dibutylphosphopentene-3.

B.p. 190-191° (7 mm); n_D^{20} 1.4478; d_4^{20} 0.9685. 0.1420 g substance: 13.0 ml NaOH (T = 0.02085). 0.1536 g substance: 14.2 ml NaOH. Found %: P 8.94, 9.03. $C_{17}H_{35}O_4P$. Calc. %: P 9.28.

Action of 1-methoxy-5-chloropentene-3 on Magnesium diethylphosphite. An ether solution of ethylmagnesium bromide, prepared from 8 g of magnesium and 37 g of ethyl bromide, was slowly added, with vigorous stirring, to 46 g of diethylphosphorous acid. Ethane was liberated during this addition, and the reaction mass grew warm. 40 ml. of anhydrous benzene and 45 g of 1-methoxy-5-chloropentene-3 were added to the magnesium diethylphosphite thus prepared. The ether was then driven off, and the mixture heated on a water bath for 3 hours. The reaction products were treated with water and dilute hydrochloric acid and extracted several times with ether. The ether and the benzene were driven off, and the residue fractionated in vacuo. This yielded 15.6 g of the unreacted

1-methoxy-5-chloropentene-3, 4 g of diethylphosphorous acid, and 12.3 g of 1-methoxy-5-diethylphosphopentene-3 with the following constants: b.p. 150-152° (11 mm); n_D^{20} 1.4471; d_4^{20} 1.0382. The 1-methoxy-5-diethylphosphopentene-3 we had prepared by reacting sodium diethylphosphite with 1-methoxy-5-chlorpentene-3 had the following constants: b.p. 146-147° (8 mm); n_D^{20} 1.4480; d_4^{20} 1.0380.

Action of 1-butoxy-5-chloropentene-3 on magnesium diethylphosphite. A Grignard reagent prepared from 2 g of magnesium, 9 g of ethyl bromide, and 150 ml of absolute ether, was gradually added to 11 g of diethylphosphorous acid. Then 35 ml of absolute benzene and 15 g of 1-butoxy-5-chloropentene-3 were added to the resultant magnesium salt. The ether and part of the benzene were driven off, and the reaction mixture was heated on a water bath for 3 hours. Processing and fractionation of the reaction mixture yielded 2 g of the original chloride, 3 g of diethylphosphorous acid, and 3.1 g of 1-butoxy-5-diethylphosphopentene-3 with the following constants: b.p. 169° (9 mm); n_D^{20} 1.4462; d_4^{20} 0.9916. The residue in the flask consisted of a tacky yellow nondistillable mass.

Action of 1-methoxy-3-chloropentene-4 on magnesium diethylphosphite. A Grignard reagent, prepared from 2 g of magnesium, 9 g of ethyl bromide, and 100 ml of absolute alcohol, was added to 11 g of diethylphosphorous acid. Then 40 ml of absolute benzene and 12 g of 1-methoxy-3-chloropentene-4 were added to the reaction mixture. The ether and part of the benzene were driven off, and the residue was heated on a water bath for 3 hours. Processing and fractionation of the reaction mixture yielded 7 g of a fraction that distilled up to 50° at 14 mm, 4 g of a fraction that distilled at 50-76° (11 mm), and 3.5 g of 1-methoxy-5-diethylphosphopentene-3 with the following constants: B.p. 150-152° (11 mm); n_D^{20} 1.4442; d_4^{20} 1.0383. The residue left in the flask was a solid, hyaline type of resin. Refractionation of the first two fractions yielded 4.5 g of the original chloride and 3 g of a fraction that distilled at 58-69° (10 mm).

Action of 1-butoxy-3-chloropentene-4 on magnesium dibutylphosphite. The reaction resembled the one described in the foregoing test, the Grignard reagent being prepared from 3 g of magnesium, 14 g of ethyl bromide, and 150 ml of absolute ether. It was added to a solution of dibutylphosphorous acid, after which 45 ml of benzene and 22 g of 1-butoxy-3-choropentene-4 were poured into the reaction mixture. Processing and fractionation of the reaction mixture yielded 5 g of the original chloride and 7 g of a fraction that distilled at 65-70° (10 mm); the residue consisted of 13 g of a transparent yellow resin.

Tests to determine the amount of ethane evolved in the reaction of ethylmagnesium bromide with diethylphosphorous acid. A Grignard reagent with a total volume of 200 ml was prepared from 10 g of magnesium, 48 g of ethyl bromide, and 150 ml of absolute ether. According to the equation:

$$(C_2H_5O)_2POH + C_2H_5MgBr \rightarrow (C_2H_5O)_2P\begin{matrix}=O\\ <\\ MgBr\end{matrix} + C_2H_6$$

1.4 g of diethylphosphorous acid should have been consumed for 5 ml of the Grignard reagent containing 0.24 g of Mg, and 225 ml of ethane should have been evolved.

The tests were run as follows: the diethylphosphorous acid was added a drop at a time to a measured volume of the Grignard reagent, the ethane given off being measured in a buret. The results are listed in the table.

Test No.	Ml of Grignard reagent	Grams of diethylphosphorus acid consumed		Ml of ethane	
		Theoretical	Actual	Theoretical	Actual
1	5	1.4	0.46	225	73
2	10	2.8	0.70	450	113
3	20	5.6	1.8	900	295

SUMMARY

1. A study has been made of the action of sodium and magnesium salts upon the isomeric butoxy- and methoxychloropentenes.

2. It has been shown that the magnesium salts of dialkyl phosphorous acids may be employed to synthesize phosphinic esters.

3. The reactions of sodium and magnesium salts of dialkyl phosphorous acids with primary butoxychloropentene are normal, no rearrangement being involved; Their reactions with the secondary butoxychloropentenes, on the other hand, involve a complete allyl rearrangement, yielding alkoxy dialkyl phosphopentenes whose structure is the same as those prepared from the primary chlorides.

LITERATURE CITED

[1] A. N. Pudovik and B. A. Arbuzov, Bull. USSR Acad. Sci. Div. Chem. Sci. 1949, No.5, 522.

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RESEARCH ON TERTIARY ALCOHOLS CONTAINING A CYCLOBUTYL RADICAL

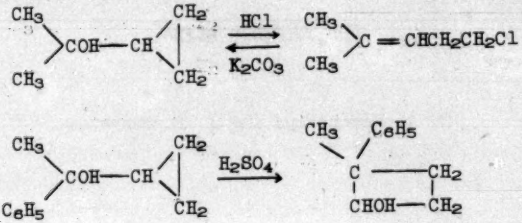
I. THE REACTION OF DIISOPROPYLCYCLOBUTYLCARBINOL WITH HYDROCHLORIC AND SULFURIC ACIDS

T. A. Favorskaya and I. P. Yakovlev

Research on the polymethylene hydrocarbons and their derivatives is largely the work of Russion scientists. The basic research on the chemistry of the derivatives of cyclopropane and cyclobutane has been done chiefly by N. Ya. Demyanov and N. M. Kizhner, who established that these cyclic systems were not very stable and converted them into compounds with open chains of carbon atoms or into more stable compounds. N. M. Kizhner [1], for example, showed that the reaction of hydrobromic and hydriodic acids upon dimethylcyclobutylcarbinol, diethylcyclobutylcarbinol, and diphenylcyclobutylcarbinol involved the expansion of the four-membered ring to a five-membered one. N. Ya. Demyanov [2] was the first to show that the action of concentrated HBr on cyclopropylcarbinol resulted in the formation of isomerization products - bromocyclobutane and 2-bromobutene-3 - in addition to the normal reaction product - cyclopropylbromomethane [3]. The same two isomeric bromides are formed when hydrobromic acid reacts with cyclobutanol [4]. Concentrated HBr and HI isomerize cyclobutylcarbinol to bromine and iodine derivatives of cyclopentane, while ethylcyclobutylcarbinol is isomerized and its ring is expanded when acted upon by these acids [5]. B. A. Kazansky [6] tried to dehydrate dimethylcyclobutylcarbinol with metallic sodium in decalin at 120°, without acids present. The reaction followed two lines, the cyclobutane ring being preserved. When reacted with HBr, diphenylcyclopropylcarbinol yields a bromide, to which Lipp [7] attributed the structure of diphenylcyclopropylbromomethane. Since the bromide was highly inert, N. M. Kizhner was forced to assume that the author had actually secured 1,1-diphenyl-2-bromocyclobutane, whereupon he reacted diphenylcyclobutylcarbinol with hydrobromic acid, again securing a highly inert bromide [8]. This led the author to assert that here, as in the derivatives of triphenylcarbinol, the bromine may be shifted to the phenyl radical. Apparently here, as in the bromide of diphenylcyclopropylcarbinol, the ring was enlarged, yielding 1,1-diphenyl-2-bromocyclopentane, which could explain the high inertness of the synthesized bromide.

T. A. Favorskaya has recently investigated the reaction of hydrochloric and sulfuric acids with tertiary cyclopropane alcohols: dimethylcyclopropylcarbinol [9], methylethylcyclopropylcarbinol [10], and methylphenylcyclopropylcarbinol [11]. Hydrochloric acid converts the first two of these alcohols into unsaturated

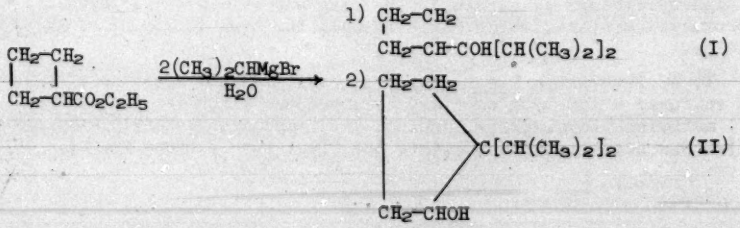
derivatives and opens the carbon ring, whereas this is supplemented by the formation of derivatives of cyclobutane in the case of methylphenylcyclopropylcarbinol.



When the chlorides prepared from dimethylcyclopropylcarbinol and methylethylcyclopropylcarbinol were heated with a potash solution, they were converted into the initial cyclic alcohols. When unsaturated chlorides prepared from methylphenylcyclopropylcarbinol were heated with an aqueous solution of an alkali, they were converted into diethylenic hydrocarbons; under these same conditions the cyclic chloride proved to be extraordinarily stable, being recovered unchanged even after 150 hours of heating. Only after the chloride had been treated with an alcoholic solution of NaOH was hydrogen chloride split off and the four-membered ring ruptured, yielding a diethylenic hydrocarbon.

The diversity of the transformations observed in the papers cited and the little research that has been done on tertiary alcohols that contain a cyclobutyl radical led us to undertake a study of the reaction of several alcohols of this type with hydrochloric and sulfuric acids.

We synthesized diisopropylcyclobutylcarbinol from the ethyl ester of cyclobutanecarboxylic acid and isopropylmagnesium bromide in a Grignard reaction. We observed the first recorded instance of the simultaneous formation of two isomeric cyclic alcohols, viz.: diisopropylcyclobutylcarbinol and 1,1-diisopropylcyclopentanol-2, in an organomagnesium synthesis of compounds containing a cyclic radical. The alcohol yield was practically independent of the reaction conditions, about 70% of diisopropylcyclobutylcarbinol and about 30% of 1,1-diisopropylcyclopentanol-2, based on the total alcohols synthesized, being formed in every case. Moreover, a minute quantity of an unsaturated product, which we managed to process with a $KMnO_4$ solution, was always found in the alcohols.



The oxidation products of the unsaturated compound found in the alcohols yielded formic and oxalic acids. It is difficult to form an idea of the structure of the unsaturated compound from the formation of these two acids. The syntheses of dimethyl-, diethyl-, and diphenylcyclobutylcarbinols apparently do not result in the formation of isomeric alcohols and unsaturated products, since there are no references thereto in the literature. The organomagnesium complex was carefully decomposed with pieces of ice, and the ether layer that separated was decanted, the isomerization of the previously prepared diisopropylcyclobutylcarbinol into 1,1-diisopropylcyclopentanol-2 occurring only when the action of the acids upon the initial alcohol is fairly energetic. It must therefore be admitted that the isomeric alcohol was formed by the isomerization of the organomagnesium complex at the instant of its formation.

The structure of the synthesized alcohols was established by oxidizing them with a chromic acid mixture. Oxidation of diisopropylcyclobutylcarbinol yielded cyclobutanecarboxylic acid; in one run diisopropylcyclopentanol-2 yielded the hydroxy acid $HO_2CCH_2CH_2CH_2C(OH)[CH(CH_3)_2]_2$, which was isolated as the lactone with a b.p. of 80-83°, and in another α,α-diisopropylglutaric acid $HO_2CCH_2CH_2C(CO_2H)[CH(CH_3)_2]_2$ with a m.p. of 168-170° being produced. The hydroxycarboxylic acid was produced when the chromic acid mixture was poured into the alcohol, the dicarboxylic acid being produced when the alcohol was poured into the chromic acid. The former resulted from rupture of the ring at the 1,2 position, the latter from ring rupture at the 2,3 position.

Heating diisopropylcyclobutylcarbinol to 100° for 6 hours with 25% sulfuric acid yielded no isomerization product, though partial isomerization to diisopropylcyclopentanol-2 took place when 50% sulfuric acid was employed. The principal reaction product was the unsaturated hydrocarbon diisopropylmethylenecyclobutane (25-30% of the initial alcohol by weight). The reaction involved considerable tarring.

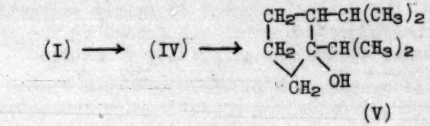
$$(I) \longrightarrow \underset{(III)}{CH_2{-}CH_2 \;\; CH_2{-}C{=}C[CH(CH_3)_2]_2} + (II)$$

Diisopropcyclcyclobutylcarbinol did not react with 18% hydrochloric acid, but when an excess of a 36% acid was used, the chloride (IV) was the principal reaction product, plus an unsaturated hydrocarbon that was identical with the hydrocarbon secured in the reaction of diisopropylcyclobutylcarbinol with sulfuric acid, and an isomeric alcohol, diisopropylcyclopentanol-2, which was identical with the alcohol produced in the organomagnesium synthesis and in the reaction with sulfuric acid.

$$(I) \xrightarrow{HCl} \underset{(IV)}{CH_2{-}CH(CH_3)_2 \;\; CH_2{-}CH_2{-}C(Cl){-}CH(CH_3)_2} + (II) + (III)$$

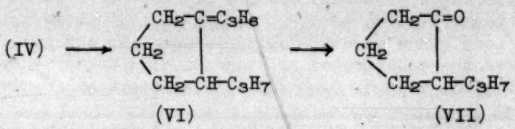
Reacting 1,1-diisopropylcyclopentanol-2 with 36% HCl under the same conditions as those used for diisopropylcyclobutylcarbinol yielded the chloride (VIII), b.p. 66-67° (19 mm), and the chloride (IX), b.p. 110° (18 mm).

The percentage of chlorine, determined by the Carius method, was the same in all the three chlorides, being equivalent to one atom of chlorine per molecule of the compound. Efforts to saponify the chlorides (VIII) and (IX) with potash met with failure. The chloride (IV), on the other hand, was saponified readily, yielding the alcohol 1,2-diisopropylcyclopentanol-1. The chloride (IV) is a five-membered cyclic compound, produced by the isomerization of the four-membered ring to a five-membered one and the shift of one isopropyl group from the 1,1 position to the 1,2 position:



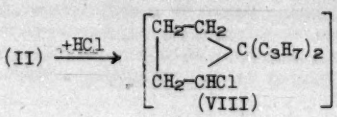
(V)

As a matter of fact, splitting elements of hydrogen chloride from this chloride with sodium ethylate yielded an unsaturated hydrocarbon that differed appreciably from the other hydrocarbons synthesized. In view of the danger of having a trace of other unsaturated hydrocarbons, it was not distilled with sodium although it contained traces of the chloride (Beilstein test). Ozonization of the hydrocarbon yielded isopropylcyclopentanone, the semicarbazone of which had a m.p. of 119°. The reaction was as follows:

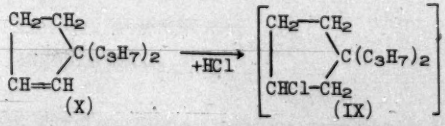


(VI) (VII)

The formation of two chlorides from diisopropylcyclopentanol is explainable on the assumption that the reaction followed three lines: 1) formation of the normal product of the substitution of chlorine for the hydroxyl group; 2) formation of an unsaturated hydrocarbon; and 3) addition of HCl at the instant the unsaturated hydrocarbon is formed, when the molecule is in an activated state, the chlorine entering at the 3 position, viz.:



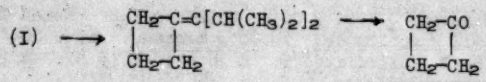
(VIII)

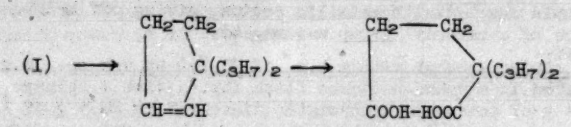


(X) (IX)

No precise determination of the position of chlorine in the chlorides (VIII) and (IX) was made, owing to the small quantities at our disposal.

When reacted with 50% sulfuric acid 1,1-diisopropylcyclopentanol yielded an unsaturated hydrocarbon with a b.p. of 74-75° at 20 mm. The hydrocarbon secured from diisopropylcyclobutylcarbinol had a b.p. of 39-42° at 19 mm. Hence, different unsaturated hydrocarbons were secured in these two cases. The structure of the synthesized hydrocarbons was established by ozonization, cyclobutanone being produced from the first one, and α,α-diisopropylglutaric acid from the second.





EXPERIMENTAL

The initial substances used in the synthesis of diisopropylcyclobutylcarbinol were the ethyl ester of cyclobutanecarboxylic acid: n_D^{21} 1.4234; $d_4^{21.5}$ 0.9538; b.p. 157-161° (prepared from cyclobutanecarboxylic acid), and isopropyl bromide. All our efforts to secure a high yield of the diisopropylcyclobutylcarbinol met with failure. We always obtained a mixture of two alcohols, 70% of the total being diisopropylcyclobutylcarbinol, and 30% being the five-membered cyclic alcohol 1,1-diisopropylcyclopentanol-2. The best conditions for synthesizing diisopropylcyclobutylcarbinol were as follows.

1 mol of isopropyl bromide in 200 ml of ether was added a drop at a time to 1 mol of magnesium shavings in the vessel ordinarily used for organomagnesium synthesis, fitted with a stirrer and well-chilled, after which a solution of 0.5 mol of the ethyl ester of cyclobutanecarboxylic acid in 60 ml of ether was added. When all the ether had been added, the reaction mixture was heated on a water bath to a gentle boil for an hour, after which it was cooled with water, and the organomagnesium complex was decomposed with pieces of ice. The ether layer was decanted, and the basic magnesium bromide decomposed with dilute (1:5) hydrochloric acid and extracted with ether, the ether extract being washed once each with a soda solution and with water and then combined with the bulk of the ether and dried over Na_2SO_4. The ether was then driven off, and the resultant product fractionated into a column (at 9.5 mm), two alcohols being isolated: 18 g of one with a b.p. of 60-62°, and 5 g of another with a b.p. of 84-88°. The residue totaled 6 g of tar, while 23 g of the ethyl ester of cyclobutanecarboxylic acid was recovered unchanged. The alcohols contained an unsaturated impurity, which was eliminated by treatment with a 1% $KMnO_4$ solution.

One alcohol, diisopropylcyclobutylcarbinol, was a mobile liquid with a barely perceptible yellowish tinge and the typical odor of tertiary alcohols. It did not react with phthalic anhydride.

B.p. 60-61° at 9.5 mm, 161-165° at 756 mm; $n_D^{18.5}$ 1.4495; ω_{FCD} 21.2. d_4^9 0.9125; $d_4^{22.4}$ 0.8915; MR_D 51.66; Calculated 52.32.

0.1054 g substance: 0.2970 g CO_2; 0.1315 g H_2O. 0.1310 g substance: 0.3682 g CO_2; 0.1620 g H_2O. Found %: C 76.85, 76.65; H 13.86, 13.74.

0.0503 g substance; 20.70 g benzene; Δt 0.071°. Found: M 171.3. $C_{11}H_{22}O$. Calculated %: C 76.87; H 13.81. M 171.5.

The other alcohol, 1,1-diisopropylcyclopentanol-2, was a less highly mobile liquid with a faint peppermint odor. It reacted with phthalic anhydride to form a derivative with a m.p. of 185°.

B. p. 83-86° at 9.5 mm; $n_D^{21.3}$ 1.4591; ω_{FCD} 19.6; d_4^0 0.9276; $d_4^{21.3}$ 0.9098; MR_D 51.15; Calculated 52.32.

0.1777 g substance: 0.4991 g CO_2; 0.2201 g H_2O. Found %: C 76.83; H 13.86. 0.0412 g substance; 18.08 g benzene: Δt 0.064°. Found %: M 171.0. $C_{11}H_{22}O$. Calculated %: C 76.87; H 13.81. M 171.5.

Both alcohols reacted with metallic sodium, giving off hydrogen. A test for the presence of a carbonyl group was negative

Oxidation of the alcohol with a b.p. of 83-86° at 9.5 mm. 4 g of the alcohol was placed in a round-bottomed flask fitted with a stirrer, and a mixture of 19.4 g of potassium bichromate, dissolved in 24.5 g of H_2SO_4 (1.84), and 80 ml of water was added drop by drop at room temperature. After two hours of oxidation, the temperature was raised to 80°. Then the mixture was heated to 90° for another 3 hours. After the reaction mixture had cooled and been diluted with 100 ml of water, the reaction product was extracted with benzene and dried over Na_2SO_4, the 2.3 g of the resulting product being fractionated in vacuo. This yielded a fraction with a b.p. of 80-83° at 9 mm, which did not react with phenylhydrazine, but slowly dissolved in alkali. The neutralization equivalent was determined by back-titration.

0.1561 g substance: 19.0 ml NaOH; 7.9 ml HCl (T_{NaOH} 0.003505; T_{HCl} 0.004223). Found: equiv. 206.9. $C_{11}H_{22}O_3$. Calculated: equiv. 202.7.

These findings are evidence of the formation of a hydroxy acid; oxidation of 1,1-diisopropylcyclopentanol-2 could yield the hydroxy acid δ,δ'-diisopropyl-δ-hydroxyvaleric acid. When the alcohol was added to the chromic acid mixture, a dicarboxylic acid with a m.p. of 168-170° was produced instead of the hydroxy acid.

0.0920 g substance: 10 ml NaOH; 0.2 ml H_2SO_4. 0.1098 g substance: 14.0 ml NaOH; 1.4 ml H_2SO_4 (T_{NaOH} 0.003505; $T_{H_2SO_4}$ 0.005428). Found: equiv. 108.5, 106.5. $C_{11}H_{20}O_4$. Calculated: equiv. 108.8. 0.0671 g substance: 0.0332 g Ag. 0.1551 g substance: 0.0768 g Ag. Found %: Ag 49.60, 49.70. $C_{11}H_{18}O_4Ag_2$. Calculated %: Ag 50.02.

The analysis of the silver salt and the neutralization equivalent of this acid indicate that it is 2,2-diisopropylglutaric acid, which could result from rupture of the five-membered ring between the CHOH and CH_2 groups. The structure of this acid was not confirmed by synthesizing it. The silver salt of α,α'-diisopropylglutaric acid is fairly freely soluble in water.

Oxidation of the alcohol with a b.p. of 60-61° at 9.5 mm. In this oxidation we used 4 g of the alcohol, 19.4 g of potassium bichromate, 40 ml of water, and 24.5 g of sulfuric acid (sp. gr. 1.84), the alcohol being added to a hot solution of the oxidizing mixture. Heat was evolved in the reaction, so that the flask had to be chilled. After all the alcohol had been added, the mixture was heated to 55-60° until the alcohol odor had disappeared, after which it was cooled, diluted with 150 ml of water, extracted with ether, dried over Na_2SO_4, and fractionated.

This yielded cyclobutanecarboxylic acid with a b.p. of 95° at 16 mm, which agrees with the figure given in the literature (95° at 15 mm).

Found: M 110.0. $C_5H_8O_2$. Calculated: M 100.0. Found %: Ag 51.70, 51.00. $C_5H_7O_2Ag$. Calculated: Ag 51.8.

Reaction of diisopropylcyclobutylcarbinol with sulfuric acid. Preliminary experiments with 25% sulfuric acid showed that the alcohol was not isomerized.* Nor did 50% produce isomerization at 50°, all the alcohol being recovered unchanged. But when the temperature of the reaction mixture was raised to 100°, the alcohol did react, 18 g of the alcohol yielding 1.5 g of an unsatured hydrocarbon with a b.p. of 42-46° at 24 mm, 1.5 g of 1,1-diisopropylcyclopentanol-2 with a b.p. of 84° at 9 mm, 4 g of tar, and 6 g of the initial alcohol. The contact time was 6 hours in all the runs.

The unsaturated hydrocarbon, diisopropylmethylenecyclobutane, was a highly mobile liquid that smelled like kerosene. After the hydrocarbon had been distilled with sodium, it had a b.p. of 128-129° at 757 mm.

$n_D^{21.8}$ 1.4487; ω_{FCD} 24.2; d_4^0 0.8119; $d_4^{21.8}$ 0.7950; MR_D 51.79; Calculated: 50.33.

0.0501 g substance: 0.1596 g CO_2; 0.0613 g H_2O. 0.0533 g substance: 0.1701 g CO_2; 0.0621 g H_2O. Found %: C 86.93, 87.15; H 13.53, 12.74. 0.0163 g substance; 16.58 g benzene: Δt 0.032°. 0.0477 g substance; 16.58 g benzene: Δt 0.093°. Found: M 156.3, 160.5. $C_{11}H_{20}$. Calculated %: C 86.84, H 13.15. M 153.5.

After the isomeric alcohol 1,1-diisopropylcyclopentanol-2 had been carefully fractionated, it had a sharp boiling point of 120° at 19 mm (0.95 g); n_D^{21} 1.4580; ω_{FCD} 19.8; d_4^{21} 0.9100; MR_D 51.0; Calculated 52.32. The constants of the isomeric alcohol were the same as those of the 1,1-diisopropylcyclopentanol produced during the synthesis of diisopropylcyclobutylcarbinol.

Reaction of diisopropylcyclobutylcarbinol with hydrochloric acid. The alcohol did not react with 18% hydrochloric acid at 100°. When reacted with 36% hydrochloric acid at room temperature for 36 hours, the alcohol yielded an unsaturated hydrocarbon, the chloride (IV), and an alcohol. The constants of the unsaturated hydrocarbon and of the alcohol corresponded with those of the diisopropylmethylenecyclobutane and the 1,1-diisopropylcyclopentanol-2, respectively, synthesized in the reaction of the alcohol with sulfuric acid.

0.0303 g substance; 16.55 g benzene: Δt 0.062°. 0.0753 g substance; 16.55 g benzene: Δt 0.153°. Found: M 148.7, 149.5. $C_{11}H_{20}$. Cal- M 153.5.

The chloride (IV) was a barely yellowish, mobile liquid.

B.p. 64.66° at 17 mm; $n_D^{19.4}$ 1.4511; ω_{FCD} 19.5; $d_4^{19.4}$ 0.9037; MR_D 55.34; Calculated. 55.48.

*The solutions of hydrochloric and sulfuric acids were prepared from a mixture of equal parts of water and ethyl alcohol, and the corresponding weight of the concentrated acid (sp. gr. 1.84 for the sulfuric and 1.19 for the hydrochloric acid).

0.3162 g substance: 0.2320 g AgCl. 0.3524 g substance: 0.2616 g AgCl. Found %: Cl 18.15, 18.36. $C_{11}H_{21}Cl$. Calculated %: Cl 18.64.

Saponification of the chloride (IV). 3.4 g of the chloride was heated to boiling with 40 ml of a 10% potash solution for 20 hours. Processesing of the saponification product and vacuum fractionation yielded 0.5 g of an alcohol with a b.p. of 105-108° at 17 mm; $n_D^{19.5}$ 1.4567; ω_{FCD} 18.8. The synthesized alcohol did not react with phthalic anhydride. The structure of the synthesized alcohol was not established nor was it analyzed, owing to the small quantity obtained. But in view of the fact that the chloride (IV) yielded the unsaturated hydrocarbon (VI) and that the latter yielded the ketone (VII), it must be assumed that the alcohol synthesized by saponification was a tertiary, five-membered alcohol. This is supported by the boiling point and the n_D and ω_{FCD}. Its tertiary nature is indicated by its inertness toward phthalic anhydride. A secondary alcohol reacted with phthalic anhydride, as we have seen.

Reaction of 1,1-diisopropylcyclopentanol-2 with 36% hydrochloric acid. 60 ml of 36% hydrochloric acid was added to 12 g of the alcohol, and the mixture was allowed to stand at room temperature for two days. Then the mixture was poured into 150 ml of water. The reaction product was extracted with ether, dried over Na_2SO_4, and fractionated in vacuo. The two chlorides (VIII) and (IX) were isolated.

The chloride (VIII) was a highly mobile liquid with a rather fragrant odor.

B.p. 66-67° at 19 mm; $n_D^{19.4}$ 1.4575; ω_{FCD} 19.7; d_4^0 0.8954; $d_4^{19.4}$ 0.8815; MR_D 58.33; Calculated 55.48.

0.2430 g substance: 0.1802 g AgCl. 0.3215 g substance: 0.2382 g AgCl. Found %: Cl 18.30, 18.33. $C_{11}H_{21}Cl$. Calculated %: Cl 18.64.

The chloride (IX) was a slightly mobile yellowish liquid with an unpleasant odor.

B.p. 110° at 18 mm; $n_D^{19.5}$ 1.4767; ω_{FCD} 19.6; d_4^0 0.9775; $d_4^{19.5}$ 0.9642; MR_D 55.65; Calculated 55.48.

0.2747 g substance: 0.3026 g AgCl. 0.2060 g substance: 0.2180 g AgCl. Found %: Cl 18.34, 17.87. $C_{11}H_{21}Cl$. Calculated %: Cl 18.64.

Saponification of the chlorides (VIII) and (IX). Saponification was conducted for 48 hours with a 20% potash solution at the boiling points of the solutions, but we were unable to saponify the chlorides. The physical constants of the reaction products were the same as those of the initial chlorides.

Reaction of 1,1-diisopropylcyclopentanol-2 with sulfuric acid. 5 g of the alcohol was heated to 80-85° for 12 hours with 10 ml of 50% H_2SO_4. Then the mixture was diluted with 50 ml of water. The reaction product was extracted with ether, dried over Na_2SO_4, and fractionated, yielding an unsaturated hydrocarbon.

B p. 74-75° at 20 mm; $n_D^{19.5}$ 1.4562; ω_{FCD} 23.1; d_4^0 0.8390; $d_4^{19.5}$ 0.8243; MR_D 50.64; Calculated 50.33. 0.0712 g substance: 0.2277 g CO_2; 0.0869 g H_2O. Found %: C 87.27; H 13.35. 0.0151 g substance; 16.5 g benzene: Δt 0.031°. 0.0127 g substance; 16.5 g benzene: Δt 0.029°. Found: M 151.5, 159.5. $C_{11}H_{20}$. Calculated %: C 86.84; H 13.15. M 156.1.

Ozonolysis of the unsaturated hydrocarbons. 1.2 g of the unsatured hydrocarbon secured from diisopropylcyclobutylcarbinol and 1.3 g of the hydrocarbon secured from 1,1-diisopropylcyclopentanol-2 were ozonized, the 2.5 g of hydrocarbons requiring 0.77 g of ozone. The ozone was passed through at 0.00535 g

per minute. After 2.5 hours had elapsed the percentage of ozone was practically identical at the inlet and outlet ends of the apparatus, which indicated that the reaction was complete. The chloroform was removed from the ozonization product by means of a capillary in vacuo. The ozonization product was decomposed with water, yielding cyclobutanone with a b.p. of 90-110° (the literature gives the b.p. of cyclobutanone as 100° at 760mm) and α,α-diisopropylglutaric acid, which we did not manage to crystallize, although its consistency was very thick. We also secured a minute amount of a substance with a b.p. of 130-145°, the nature of which we were unable to determine. This must be diisopropyl ketone (b.p. 124.5°) with a minute trace of hydrocarbons that prevented the isolation of the semicarbazone in the crystalline state.

The semicarbazone of the cyclobutanone melted at 195-202° with decomposition, which agrees with the figure given in the literature.

Found %: N 33.88. $C_5H_9ON_3$. Calc. %: 33.05. 0.3316 g substance: 34.4 ml NaOH (T 0.003515). 0.1882 g substance: 20.0 ml NaOH; 0.8 ml HCl (T 0.004197). Found: equiv. 116.0, 106.8. $C_{11}H_{20}O_4$. Calc. equiv. 108.0. 0.1142 g substance: 0.0551 Ag. 0.1346 g substance: 0.0652 g Ag. Found %: Ag 48.24, 48.44.* $C_{11}H_{18}O_4Ag_2$. Calc. %: Ag 50.02.

Splitting HCl from the chloride (IV). 12.2 g of the chloride (IV) was refluxed for 6 hours with 17 g of sodium ethylate in 30 ml of ethyl alcohol. The reaction product was diluted with 80 ml of water, extracted with ether, and dried over $MgSO_4$. Repeated fractionation yielded 4.8 g of a hydrocarbon.

B.p. 46.5-48.5 at 10 mm; n_D^{20} 1.4446; ω_{FCD} 20.6; d_4^0 0.8189; d_4^{20} 0.8023; MR_D 50.38; Calc. 50.33.

0.1218 g substance: 0.3935 g CO_2; 0.1417 g H_2O. 0.1279 g substance: 0.4024 g CO_2; 0.1481 g H_2O. Found %: C 86.91, 86.70; H 13.02, 12.96. 0.0456 g subs.: 17.30 g benzene; Δt 0.110°. 0.0548 g substance; 17.30 g benzene: Δt 0.110°. Found: M 145.8, 145.0. $C_{11}H_{20}$. Calc. %: C 86.84; H 13.5 M 152.

Ozonization of the hydrocarbon yielded 2-isopropylcyclopentanone. The melting point of the ketone's semicarbazone was 119°.

0.0786 g substance: 15.5 ml N_2 (19.3°, 758.5 mm). 0.1080 g substance: 21.3 ml N_2 (19.2°, 758.5mm) Found %: N 22.70, 22.86. $C_9H_{17}ON_3$. Calc. %: N 22.94.

Analysis thus clearly shows that the reaction of diisopropylcyclobutylcarbinol with concentrated hydrochloric acid expands the ring and shifts one isopropyl group from the 1 position to the 2 position.

SUMMARY

1. The following compounds have been synthesized and identified for the first time: diisopropylcyclobutylcarbinol; 1,1-diisopropylcyclopentanol-2; diisopropylmethylenecyclobutane; 1,1-diisopropylcyclopentene-2; 1,2-diisopropyl-1-chlorocyclopentane; and 1,2-diisopropylmethylenecyclopentane.

2. It has been shown that the reaction of diisopropylcyclobutylcarbinol with sulfuric acid follows two lines: 1) dehydration without any isomerization; and 2) dehydration with the production of an isomeric alcohol – 1,1-diisopropylcyclopentanol-2.

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*The low percentage of Ag is due to failure to wash the silver salt of the acid with ether.

3. Three compounds are formed in the reaction of diisopropylcyclobutylcarbinol with hydrochloric acid: 1,1-diisopropylcyclopentanol-2; diisopropylmethylenecyclobutane; and 1,2-diisopropyl-2-chlorocyclopentane.

4. 1,1-Diisopropylcyclopentanol-2 is dehydrated by sulfuric acid as well as by hydrochloric acid, yielding 1,1-diisopropylcyclopentene-2, the reaction with the latter acid also yielding two five-membered cyclic chlorides, one of them apparently the product of a secondary reaction.

5. The isomerization of one ring compound into another in an organomagnesium synthesis has been observed for the first time. In the synthesis of diisopropylcyclobutylcarbinol, for example, 1,1-diisopropylcyclopentanol-2 is formed at the same time. The formation of the isomeric alcohol must be the result of isomerization of the organomagnesium complex.

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RESEARCH ON TERTIARY ALCOHOLS CONTAINING A CYCLOBUTYL RADICAL

II. THE REACTION OF METHYLPHENYLCYCLOBUTYLCARBINOL WITH HYDROCHLORIC AND SULFURIC ACIDS

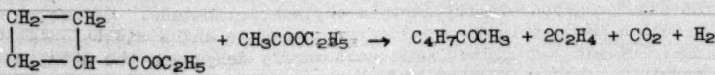
T. A. Favorskaya and I. P. Yakovlev

In our preceding report [1] we showed that sulfuric and hydrochloric acids dehydrate diisopropylcyclobutylcarbinol and also isomerize it to a five-membered ring. It was also found that the formation of the normal reaction product in the synthesis of diisopropylcyclobutylcarbinol from the ethyl ester of cyclobutanecarboxylic acid is paralleled by the formation of its isomeric alcohol – 1,1-diisopropylcyclopentanol-2 – as the result of isomerization of the organomagnesium complex itself.

After dealing with diisopropylcyclobutylcarbinol we decided to investigate the reaction of tertiary alcohols that contained a phenyl radical and a cyclobutyl radical with hydrochloric and sulfuric acids. In alcohols of this structure one of the transformations suffered by the alcohols was eliminated, i.e. the formation of a phenyl group, which facilitated proof of the structure of the resultant products. Three such alcohols were chosen for our research: methylphenylcyclobutylcarbinol, ethylphenylcyclobutylcarbinol and isopropylphenylcyclobutylcarbinol.

Methyl cyclobutyl ketone was synthesized by N. M. Kizhner [2] by means of an organomagnesium synthesis from cyclobutanecarboxamide, but he failed to describe it, giving only its boiling point. Kolman and Perkin [3] synthesized it from the calcium salt of cyclobutanecarboxylic acid, the yield being poor, while Perkin and Sinkler [4] synthesized it from the acid chloride of this acid, the yield being 60-65%. Ethyl cyclobutyl ketone and isopropyl cyclobutyl ketone were synthesized by N. D. Zelinsky and his associates [5,6] by passing cyclobutane carboxylic acid with propionic and isobutyric acids over ZnO and MnO catalysts, their yields being 55 and 37% of the theoretical, respectively.

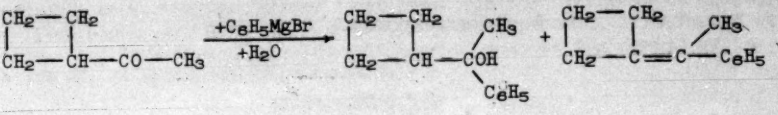
An endeavor made during the course of the present research to synthesize cyclobutyl phenylketone over a chrome-manganese catalyst, using cyclobutanecarboxylic acid and a mixture of benzoic acid and ethyl benzoate, was unsuccessful. On the other hand, the synthesis of methyl cyclobutyl ketone was successful. A mixture of 1:3 parts by volume of cyclobutanecarboxylic and acetic acids was used for catalysis. The ketone yield was 50%. The yield was raised to 63% however, when the ethyl esters of these acids were used instead of the acids themselves, the proportions remaining the same. The reaction was as follows:



$$\begin{array}{l} CH_2{-}CH_2 \\ \quad | \quad\quad | \\ CH_2{-}CH{-}COOC_2H_5 \end{array} + CH_3COOC_2H_5 \rightarrow C_4H_7COCH_3 + 2C_2H_4 + CO_2 + H_2O$$

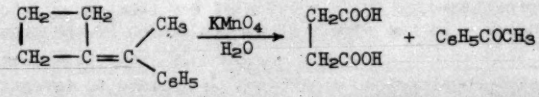
In our test 63% of methyl cyclobutyl ketone and 8.8% of dicyclobutyl ketone were produced in a single pass. The excess ethyl acetate yielded 40% acetone and 5% acetic acid, the rest of the ethyl acetate being recovered unchanged and being reusable without careful purification.

Methylphenylcyclobutylcarbinol was synthesized from methyl cyclobutyl ketone and phenylmagnesium bromide, but the yield was very low (9.8% of the theoretical). The principal reaction product was a saturated hydrocarbon – methylphenylmethylenecyclobutane, the yield being 17.1% of the theoretical.



(I) (II)

Cautious oxidation of the methylphenylmethylenecyclobutane with a $KMnO_4$ solution yielded acetophenone and succinic acid:



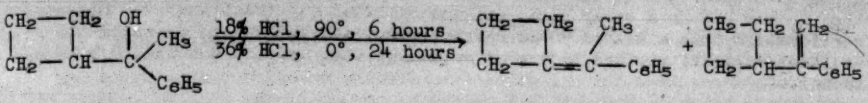
In view of the poor yield of methylphenylcyclobutylcarbinol, we abandoned its synthesis from methyl cyclobutyl ketone. It was synthesized otherwise: via cyclobutanecarbonyl chloride and phenyl cyclobutyl ketone.

Cyclobutanecarboxylic acid was prepared by the N. M. Kizhner method [7], as modified by Golmov and Kazansky [8], the yield being raised 14.8% in the first stage of the reaction (to 93% of the theoretical) and by 11% in the second stage (to 88% of the theoretical). The ethyl ester of cyclobutane-1,1-dicarboxylic acid was saponified and decarboxylated to give an 80% yield of cyclobutanecarboxylic acid. It was then converted into its acid chloride by the action of PCl_5, the yield being 78.5%. Phenyl cyclobutyl ketone was synthesized in a Friedel-Crafts reaction from the acid chloride and benzene with $AlCl_3$, the yield being 68% of the theoretical. This ketone was first synthesized by Perkin and Sinkler [9], using the same method, but their yield was 55%. The phenyl cyclobutyl ketone thus prepared served as the initial substance in our synthesis of methyl-, ethyl-, and isopropylphenylcyclobutylcarbinol.

In contrast to the synthesis of methylphenylcyclobutylcarbinol from methyl cyclobutyl ketone and phenylmagnesium bromide, synthesizing the alcohol from phenyl cyclobutyl ketone and methylmagnesium bromide produced a high yield (90% of the theoretical), no unsaturated product being formed at all. Oxidizing methylphenylcyclobutylcarbinol with a chromic acid mixture yielded acetophenone and benzoic acid.

The alcohol did not react when it was heated with 25% sulfuric acid to 90° for 6 hours. When reacted with 50% H_2SO_4 under the same conditions, it yielded an unsaturated hydrocarbon – methylphenylmethylenecyclobutane. Oxidation of the hydrocarbon with a $KMnO_4$ solution yielded acetophenone and a minute quantity of benzoic acid. 18% and 36% hydrochloric acid merely dehydrate the methylphenylcyclobutylcarbinol, two unsaturated hydrocarbons being produced at the same time: 80% of methylphenylmethylenecyclobutane and 20% of as-cyclobutylphenyl-

ethylene. The difference between their boiling points is slight, so that we must assume that the resultant fractions were not homogeneous, but contained slight traces of an isomeric hydrocarbon:



Cautious oxidation of the methylphenylmethylenecyclobutane fraction with a $KMnO_4$ solution yielded acetophenone and benzoic, succinic, and formic acids; traces of the last acid were detected by producing calomel. Ozonization of the as-cyclobutylphenylethylene yielded formic acid and phenyl cyclobutyl ketone as the principal reaction products, plus traces of acetophenone and benzoic and succinic acids.

EXPERIMENTAL

Catalytic synthesis of methyl cyclobutyl ketone. a) Preparation of the catalyst. 36.5 ml of a 26% ammonia solution was added to 60 g of chromic anhydride, and the total volume of the solution was brought up to 300 ml by the addition of water. The resultant solution was poured into 110 g of manganic nitrate dissolved in 300 ml of water, and another 36.5 ml of the 26% ammonia solution was added. The resultant brown precipitate was filtered out, washed well with water, and dried in a thermostat at 110°, after which it was decomposed by heating over a Bunsen burner in a porcelain dish with constant stirring. The decomposition process entailed the spontaneous evolution of considerable heat. The catalyst was a dark-brown, highly mobile powder. The catalyst was deposited on glass wool. The reaction was carried out in the usual catalytic apparatus, 40 g of the catalyst being used.

b) Preparation of methyl cyclobutyl ketone. 10 ml of the ethyl ester of cyclobutane carboxylic acid and 30 ml of ethyl acetate were used in catalysis, the volumetric rate of flow being 10-12 ml per hour, and the temperature 440°. This yielded 22 ml of the catalyzate. 106 ml of the ethyl ester of cyclobutanecarboxylic acid and 350 ml of ethyl acetate were processed in the same way, yielding 80 ml of acetone, 62 ml of ethyl acetate, 3 ml of acetic acid, 5 ml of the ethyl ester of cyclobutanecarboxylic acid, 60 g of methyl cyclobutyl ketone (63% of the theoretical), and 5 g of dicyclobutyl ketone.

Methyl cyclobutyl ketone was a mobile liquid with a yellowish tint and a peculiar odor.

B.p. 137-139° at 754 mm, 36° at 11 mm; n_D^{16} 1.4339; ω_{FCD} 21.1; d_4^{16} 0.9093; MR_D 28.06; Calc. 27.72.

0.0844 g substance: 0.2256 g CO_2, 0.0829 g H_2O. 0.0649 g substance: 0.1756 g CO_2, 0.0652 g H_2O. Found %: C 73.95, 73.83; H 10.77, 10.98. $C_6H_{10}O$. Cal. %: C 73.47; H 10.20.

Semicarbazone m.p. 135.5°.

0.0590 g substance: 13.7 ml N_2 (18.1°, 768 8 mm). Found %: N 27.64. $C_7H_{13}ON_3$. Cal %: N 27.09.

Synthesis of methylphenylcyclobutylcarbinol from methyl cyclobutyl ketone. 80 g of bromobenzene in 80 ml of absolute ether was slowly added to 12.4 g of magnesium, the flask being chilled with water containing snow. When all the magnesium had dissolved, a solution of 50 g of methyl cyclobutyl ketone in 200

ml of ether was added. The next day the organomagnesium complex was decomposed with water, the ether layer decanted and dried over $MgSO_4$, the residue acidulated with dilute (1:5) hydrochloric acid and extracted with ether, and the ether extract washed with water and dried over K_2CO_3. The two ether extracts were combined, the ether driven off on a water bath, and the residual oil fractionated. Repeated fractionation into a heated 50-cm herringbone dephlegmator and freezing the resultant diphenyl yielded 16.5 g of an unsaturated hydrocarbon and 10 g of an alcohol.

The unsaturated hydrocarbon – methylphenylmethylenecyclobutane – was a mobile liquid with a slight tarry odor:

B.p. 80-83° at 0.5 mm; $n_D^{12.5}$ 1.5551; ω_{FCD} 36.65; d_4^0 0.9859; $d_4^{12.5}$ 0.9743; d_4^{20} 0.9683; MR_D 52.06; Calc. 51.81.

0.1192 g substance: 16.70 g benzene: Δt 0.232°. Found: M 154.9. $C_{12}H_{14}$. Calc. M 158.0.

0.1429 g substance: 0.4743 g CO_2; 0.1147 g H_2O. 0.1422 g substance: 0.4749 g CO_2; 0.1132 g H_2O. Found %: C 90.58, 91.13; H 8.78, 8.56. $C_{12}H_{14}$. Calc. %: C 91.14; H 8.86.

Oxidation of the hydrocarbon with potassium permanganate yielded acetophenone and succinic acid. The m.p. of the acetophenone's semicarbazone was 200° its mixed melting point with a known preparation exhibiting no depression. The succinic acid had a m.p. of 182°, its mixed melting point likewise not exhibiting any depression.

The alcohol – methylphenylcyclobutylcarbinol – was a liquid with a slight tarry odor after treatment with a $KMnO_4$ solution.

B.p. 100.5-104° at 1 mm; n_D^{20} 1.5358; ω_{FCD} 27.5; d_4^0 1.0388; d_4^{10} 1.0350; d_4^{20} 1.0316; MR_D 53.72, 53.80.

0.0573 g substance; 17.45 g benzene: Δt 0.094°. 0.0455 g subs.: 17.45 g benzene: Δt 0.079°. Found: M 176.0, 163.0. $C_{12}H_{16}O$. Calc. M 178.0. 0.1713 g substance: 0.5143 g CO_2; 0.1383 g H_2O. 0.1727 g substance: 0.5186 g CO_2; 0.1409 g H_2O. Found %: C 81.93, 81.95; H 8.63, 8.92. $C_{12}H_{16}O$. Calc. %: C 81.76; H 9.15.

Synthesis of cyclobutanecarboxylic acid by the Kizhner method [7]. Synthesis of cyclobutanecarboxylic acid required the preparation of 1-bromo-3-chloropropane, malonic ester, and absolute ethyl alcohol. The reaction was carried out in stages as proposed by Golmov and Kazansky [8]. In view of the fact that our yields were better than those obtained by the foregoing authors,* we shall describe the conditions employed in our synthesis. The first stage of the synthesis was synthesizing the ethyl ester of γ-chloropropylmalonic acid. A mixture of 3 mols of malonic ester and 3 mols of 1-bromo-3-chloropropane in 500 ml of absolute ether was added in one batch to sodium ethylate, prepared from 2 mols of metallic sodium and 800 ml of absolute alcohol. The temperature of the reaction mixture was kept at 35° for four hours, and then the reaction mixture was set aside to stand for a day at room temperature (17-18°) after which 2.5 liters of water were added to the unacidulated reaction product. The oil layer was separated, and the residue extracted with ether. The oil and the ether extract were combined, washed with water, dried over Na_2SO_4, and fractionated. This yielded 93% of the theoretical yield (as against 78.5% secured by Golmov and Kazansky) of γ-chloropropylmalonic ester, with a b.p.

*The difference between our method and that of Golmov and Kazansky involve differing reaction temperature as well as a certain change in the principles of processing and isolating the reaction products.

of 142° at 10 mm. The ester was poured in one batch into a solution of sodium alcoholate in 250 ml of absolute alcohol heated to 80° (on the basis of 1 mol of sodium per mol of the ester), most of the alcohol being distilled at once on a water bath. The residue was dissolved in water and acidulated with hydrochloric acid, and the ethyl ester of cyclobutanedicarboxylic acid was extracted with ether. The yield was 88% of the theoretical (as against the 77% secured by Golmov and Kazansky).

The ethyl ester of cyclobutane-1,1-dicarboxylic acid was saponified with a 40% NaOH solution. After the resultant mixture had been acidulated and the acid recovered, it was decarboxylated by double distillation at atmospheric pressure. The overall yield after all three operations was 90% of the theoretical.

Synthesis of cyclobutanecarbonyl chloride. 490 g of cyclobutanecarboxylic acid was added a drop at a time to 1.1 kg of freshly prepared PCl_5. When the reaction, which occurred readily, was over, the reaction product was fractionated into a column in vacuo. Cyclobutanecarbonyl chloride is a highly mobile liquid with a sharp, disagreeable odor, b.p. 52-54° at 40 mm. The yield of the acid chloride was 456 g, or 78.5% of the theoretical.

Synthesis of phenyl cyclobutyl ketone. 100 g of cyclobutanecarbonyl chloride was added a drop at a time to 200 g of $AlCl_3$ in 750 ml of freshly distilled benzene. The reaction set in at 25°. The temperature of the reaction mass was gradually raised to 60° and kept there until no more HCl was liberated. After the reaction mass had cooled, the product was cautiously poured over snow and extracted with benzene, the benzene extract being washed with a soda solution and dried over $CaCl_2$. The benzene was then driven off, and the residual oil distilled with steam. The resulting ketone was distilled. B.p. 121.5-122° at 10 mm; $n_D^{20.5}$ 1.5472; ω_{FCD} 33.8; d_4^0 1.0610; d_4^{10} 1.0525; d_4^{20} 1.0440; MR_D 48.61; Calc. 47.67.

456 g of the acid chloride yielded 310 g of the ketone, or 68% of the theoretical. The ketone is a mobile canary-yellowish liquid with a pleasant odor, in low concentrations resembling that of geraniums. An ether solution of the ketone reacts exothermally with bromine, yielding a monobromo derivative with a m.p. of 61°. It slightly decolorized a solution of potassium permanganate. It does not color a ferric chloride solution. Reacted with semicarbazide it yields a semicarbazone with a m.p. of 177°.

0.2114 g substance: 0.1657 g AgBr. 0.1932 g substance: 0.1511 g AgBr. Found %: Br 33.35, 33.28. $C_{11}H_{11}BrO$. Calc. %: Br 33.46. 0.0963 g substance: 16.0 ml N_2 (19.5°, 758.0 mm). 0.0815 g substance: 13.8 ml N_2 (19.5°, 755.8 mm). Found %: N 19.35, 19.65. $C_{12}H_{15}ON_3$. Calc. %: N 19.35.

Synthesis of methylphenylcyclobutylcarbinol from phenyl cyclobutyl ketone. A solution of 20 g of methyl bromide in 200 ml of absolute ether was added portionwise from a dropping funnel, with efficient chilling and stirring, to 9.2 g of magnesium. Another 20 g of methyl bromide was passed through the solution of the organomagnesium compound as a gas. A solution of 60 g of phenyl cyclobutyl ketone in 100 ml of ether was then added drop by drop to the resultant methylmagnesium bromide, the resultant organomagnesium complex not dissolving in the ether. After all the solution had been added, the reaction mass was stirred for another 2.5 hours at room temperature, no heat being applied, and then decomposed with pieces of ice. The ether layer was decanted. The residue was acidulated with weak hydrochloric acid and extracted with ether, the ether extract being washed with a soda solution and with water, combined with the bulk of the ether layer, dried over Na_2SO_4, and fractionated. The constants

of the alcohol thus produced were exactly the same as those of the alcohol prepared from methyl cyclobutyl ketone and phenylmagnesium bromide; no unsaturated product was found in the alcohol. The yield was 59 g, or 90% of the theoretical.

Oxidation of methylphenylcyclobutylcarbinol by a chromic acid mixture. 50 g of potassium bichromate, 60 g of sulfuric acid (sp. gr. 1.84), and 200 ml of water were used in oxidizing 10 g of the alcohol. Oxidation was effected by adding the chromic acid mixture to the alcohol a drop at a time. The reaction set in at 60-67° and continued at that temperature for 3 hours. Then the reaction mixture was chilled, diluted with 200 ml of water, and extracted thoroughly with ether. The ether extract was washed with alkali and dried over $MgSO_4$. The alkali solution was acidulated with an excess of dilute (1:5) sulfuric acid and extracted with ether, the ether extract being washed with 20 ml of water and dried over $MgSO_4$. Driving off the ether from the ether extract followed by fractionation yielded 1.2 g of acetophenone (b.p. 71-74° at 8 mm). The acetophenone yielded a semicarbazone with a m.p. of 200°, its mixed melting point with the known semicarbazone exhibiting no depression. The acid portion of the reaction mixture yielded 0.6 g of benzoic acid with a m.p. of 121°, its mixed melting point with known benzoic acid exhibiting no depression.

Reaction of methylphenylcyclobutylcarbinol with H_2SO_4. a) A mixture of 15 g of the alcohol with 15 ml of 25% H_2SO_4 was heated to 90° for 6 hours, the reaction product turning slightly brown. It was extracted with ether, washed with a soda solution, and dried over $MgSO_4$. After the ether had been driven off, the 11 g of residue was distilled at 8 mm, all the product passing over in the 97-106° range. The residue of 0.5 g was not analyzed. n_D^{19} 1.5629; ω_{FCD} 37.8; d_4^{19} 0.9771; MR_D 52.53; $C_{12}H_{14}$; Calc. 51.81. The physical constants of the distilled unsaturated hydrocarbon and its chemical behavior were those of the hydrocarbon secured in the organomagnesium synthesis of the alcohol from methyl cyclobutyl ketone and phenylmagnesium bromide.

Two fractions were secured after redistillation (at 8 mm): I) b.p. 98-101°, 4.6 g; and II) b.p. 101-102°, 3.5 g.

Fraction I. n_D^{20} 1.5619; ω_{FCD} 36.6; d_4^{20} 0.9695; MR_D 52.84; Calculated 51.81. 0.0477 g substance; 16.65 g benzene: Δ t 0.090°. 0.0804 g substance; 16.65 g benzene: Δ t 0.156°. Found: M 160.0, 155.8. $C_{12}H_{14}$. Calculated: M 158.0.

Fraction II. n_D^{20} 1.5650; ω_{FCD} 38.0; d_4^{20} 0.9799; MR_D 52.52; Calculated 51.81.

0.1784 g substance: 0.5936 g CO_2; 0.1358 g H_2O. 0.1902 g substance: 0.6384 g CO_2; 0.1560 g H_2O. 0.0402 g substance; 16.15 g benzene: Δ t 0.078°. 0.0780 g substance: 16.15 g benzene: Δ t 0.151. Found %: C 90.82, 91.45; H 8.53, 9.17. M 160.2, 160.5. $C_{12}H_{14}$. Calculated %: C 91.14; H 8.86. M 158.

Oxidizing Fractions I and II with a $KMnO_4$ solution yielded acetophenone and benzoic acid. The acetophenone semicarbazone fused at 198.5° The mixed melting points of the semicarbazone and the benzoic acid with the respective known compounds exhibited no depression.

Reaction of methylphenylcyclobutylcarbinol with 18% hydrochloric acid. 15 g of the alcohol was heated to 85° for 6 hours with 20 ml of an 18% solution of hydrochloric acid. The slightly brown reaction product was extracted with ether, washed with a soda solution, and dried over Na_2SO_4. Distillation yielded two fractions (at 8 mm): I) b.p. 98-100°, 8.4 g; and II) b.p. 115-122°, 4.4 g. Fraction II was

a mixture of an unsaturated hydrocarbon and the original alcohol. Fraction I was an unsatured hydrocarbon, a highly mobile, colorless liquid with a faint odor of spruce tar: n_D^{20} 1.5585; ω_{FCD} 36.6; d_4^{20} 0.9672; MR_D 52.71; $C_{12}H_{14}$. Calculated. 51.81. The hydrocarbon was combined with the Fraction I secured in the reaction of the alcohol with 36% hydrochloric acid.

Reaction of methylphenylcyclobutylcarbinol with 36% hydrochloric acid. 16.5 g of the alcohol was poured into 36% hydrochloric acid chilled to 0° and allowed to stand at this temperature for 24 hours. Then the floating oil was removed in a separatory funnel, the acid residue being diluted with 100 ml of water and extracted with ether. The ether extract was combined with the separated oil, and the whole was washed with 20 ml of water and dried over $MgSO_4$. Driving off the ether and fractionating the residue at 8 mm yielded two fractions: I) b.p. 95-106°, 6 g; and II) b.p. 106-109°, 6.1 g.

Fraction I was combined with the hydrocarbon secured in the reaction with the 18% hydrochloric acid. Careful fractional distillation at 9 mm yielded two hydrocarbons: I) b.p. 98-100°, 12.5 g, and II) b.p. 105-107°, 3.3 g; plus III) (an intermediate fraction with a b.p. of 100-105°), 4.5 g.

Both of the hydrocarbons (Fractions I and II) were mobile, colorless liquids with the odor of fresh spruce tar

Fraction I. $n_D^{21.5}$ 1.5575; ω_{FCD} 36.8; $d_4^{21.5}$ 0.9608; MR_D 52.98; Calculated. 51.81.

0.1213 g substance: 0.4048 g CO_2; 0.0986 g H_2O. 0.1034 g substance; 0.3441 g CO_2; 0.0833 g H_2O. 0.0350 g substance; 17.35 g benzene: Δt 0.065°. 0.0648 g substance; 17.35 g benzene: Δt 0.117°. Found %: C 90.98, 90.86; H 9.08, 9.01. M 156.3, 160.4. $C_{12}H_{14}$. Calculated %: C 91.14; H 8.86. M 158.0.

Fraction II. n_D^{21} 1.5608; ω_{FCD} 37.6; d_4^{21} 0.9838; MR_D 51.98; Calculated 51.81.

0.1018 g substance; 0.3401 g CO_2; 0.0829 g H_2O. 0.1664 g substance; 0.5541 g CO_2; 0.1293 g H_2O. 0.0417 g substance; 17.05 g benzene: Δt 0.077. 0.0738 g substance; 17.05 g benzene: Δt 0.143. Found %: C 91.05, 90.70; H 9.11, 8.75. M 159.7, 152.1. $C_{12}H_{14}$ Calculated %: C 91.14; H 8.86. M 158.0.

Oxidizing Fraction I with a $KMnO_4$ solution yielded acetophenone and benzoic, formic, and succinic acids. The formic acid was detected by the formation of traces of calomel. 10 g of the hydrocarbon in 200 ml of water was used in the reaction. The $KMnO_4$ was added in small batches as it was consumed, oxidation consuming 30 g of $KMnO_4$, instead of the calculated 32.5 g. The 4.5 g of acetophenone yielded a semicarbazone with a m.p. of 201.5°. The mixed melting points of the semicarbazone, the benzoic acid, and the succinic acid with the respective known compounds exhibited no depression.

Fraction II was ozonized in chloroform, 2.8 g of the hydrocarbon being used for ozonization. After the ozonization reaction was complete, the chloroform was drawn off in vacuum. The ozonide was decomposed with water, first at room temperature and then by heating with a reflux condenser. A test with fuchsin-sulfurous acid for formaldehyde was negative. Then a solution of 4 g of soda in 10 ml of water was added to the ozonization product, and the resultant solution was boiled. The volatile products were distilled with steam (1.2 g), yielding 0.4 g of acetophenone with a b.p. of 78° at 10 mm. The semicarbazone of the

acetophenone, m.p. 200°, exhibited no depression when mixed with the known semicarbazone. The distillation residue of 0.8 g formed a weak silver mirror, and hence was processed with moist silver oxide by the Delepine method [10]. But this treatment failed to produce a positive result, since the appropriate processing yielded nothing but phenyl cyclobutyl ketone. Its semicarbazone, with a m.p. of 176°, exhibited no depression of the melting point with the known semicarbazone.

The acid products yielded benzoic acid, m.p. 120°. Distillation with steam yielded formic acid. A reaction of the first runnings of formic acid with mercuric chloride yielded an abundant precipitate, which yielded an abundant black precipitate, in turn, when a strong NaOH solution was added. After the benzoic and formic acids had been eliminated, the residue yielded succinic acid with a m.p. of 181°. The mixed melting points of the succinic and benzoic acids with the respective known compounds exhibited no depression.

SUMMARY

1. Methylphenylcyclobutylcarbinol and its dehydration products – as-phenylcyclobutylethylene and methylphenylmethylenecyclobutane – have been synthesized for the first time.

2. It has been shown that the reaction of methylphenylcyclobutylcarbinol with hydrochloric and sulfuric acids results only in its dehydration.

3. The catalytic synthesis of methyl cyclobutyl ketone from the acids and esters of the acids has been worked out, the yields running up to 63%.

4. It has been found that the yield of methylphenylcyclobutylcarbinol from phenyl cyclobutyl ketone is practically quantitative, though its yield from methyl cyclobutyl ketone is only 10%.

5. The synthesis of cyclobutanecarboxylic acid has been improved, the product yields being 93, 88, and 90% in the different reaction stages.

6. It has been found that dehydration of methylphenylcyclobutylcarbinol with sulfuric acid affects the cyclobutyl radical, dehydration with hydrochloric acid affecting the methyl group.

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THE REACTIONS OF GLYCIDOL AND ITS ETHERS WITH ACID AMIDES

III. REACTION OF GLYCIDOL ETHERS WITH ACETAMIDE

F. D. Ponomarev

Our preceding report [1] described the reaction of glycidol methyl and ethyl ethers with formamide, showing that these glycidol ethers react with formamide to yield the respective N-mono- and N,N-disubstitution derivatives of formamide. In the present report we describe the reactions of glycidol methyl and ethyl ethers with acetamide and the properties of the resultant products.

The experiments on the reaction of acetamide with these ethers were carried out at various temperatures, with heat applied for different lengths of time, with and without acid (H_2SO_4) and basic (NaOH) catalysts, with acetamide-ether ratios of 1:1, 1:2, and 2:1, and with refluxing over an oil bath or heating in sealed ampoules.

The reaction hardly takes place at all when refluxing is done at 100-130° for 5 hours. Nor does a 100%, or even a 200%, excess of acetamide produce a satisfactory result. It was found that the reaction of acetamide with glycidol ethers occurs best under pressure in sealed glass ampoules. Under these conditions two products are formed as a rule: N-mono- and N,N-disubstitution derivatives of acetamide and its polymer. There were no advantages in carrying out the reaction in toluene. Nor was any advantage found in experiments in which the ether was used in excess (2 mols) or when prolonged heating (12 hours) was employed. These conditions, as well as a higher temperature (165°), result in a decrease in the product yield and an increase in the polymer yield.

It should be noted that acetamide does not react with glycidol ethers as readily as does formamide. The best results were usually secured in the reaction of acetamide with the glycidol ethers when the following procedure was used. The acetamide was placed in a refractory tube with a 20% excess of the glycidol ether over the theoretical and 2-3 drops of NaOH. The tube was sealed and heated on an oil bath at 150° for 10 hours. When the tube was opened, no gaseous products were found, as a rule. After this heating period, the reaction mixture was an oily, homogeneous, light or dark-brown liquid. Chilling it (to -10°) caused part of the unreacted amide to settle out; it was filtered out, and the reaction mixture was processed three times with ether (25-ml batches) to eliminate the amide completely. Then the ether was driven off on a water bath, and the reaction product was vacuum-distilled two or three times. In every case a residue (18-20%) was left within the flask as a faintly or brightly colored polymer after the reaction product had been distilled.

All the alkoxy hydroxy amides we produced were liquids with a specific odor, which were freely soluble in alcohol and ether. The constants of the synthesized substances are given in the table.

Substance	Boiling Point at 8 mm	d_4^{15}	n_D^{15}	MR_D	
				Calc.	Found
$CH_3CONH-CH_2-CHOH-CH_2OCH_3$	97-105°	1.0876	1.4461	36.69	36.09
$CH_3CONH-CH_2-CHOH-CH_2OC_2H_5$	122-125	1.0605	1.4450	41.19	40.41
$CH_3CON(CH_2-CHOH-CH_2OCH_3)_2$	158-165	1.0775	1.4482	58.87	58.46
$CH_3CON(CH_2-CHOH-CH_2OC_2H_5)_2$	165-170	1.0524	1.4471	67.90	66.91

We have also investigated the reactions of these glycidol ethers with ethanesulfonamide and benzenesulfonamide. Experiments with these amides, run under various conditions, like those with acetamide, either failed to yield any satisfactory results at all or else, when we did manage to isolate the N-mono- or N,N-disubstitution derivative of ethanesulfonamide, the minute quantities obtained made it impossible to identify them in detail (the percentage of nitrogen was determined by the Kjeldahl method).

One of the outstanding chemical properties of N-mono- and N,N-disubstitution derivatives of acetamide is their instability. They turn yellow in storage, decomposing, even though only slowly. Their decomposition is quicker when they are acted upon by solid alkalies at room temperature, the sharp odor of ammonia being manifested, particularly when the products are distilled over solid KOH in vacuo.

EXPERIMENTAL

A commercial preparation of acetamide (m.p. 80°) was employed in the reaction; the glycidol ethers were prepared from glycerol by the method described in the preceding communication [1], the sole change being that the ethers of glycerol α-monochlorohydrin were prepared with a boron fluoride etherate as a catalyst by the method described by A. A. Petrov [2] for synthesizing the methyl ether of glycerol α-monochlorohydrin. An 800% excess of absolute methanol or ethyl alcohol and 0.5-0.8 mg of boron fluoride etherate were added to 0.2 mol of epichlorohydrin (b.p. 115-119°) chilled to -10°. The bottle was left to stand in the -10° freezing mixture. After 2 hours had elapsed, the contents of the bottle were fractionated with a three-bulb dephlegmator. The reaction is thus 4 to 5 times faster when $BF_3 \cdot (C_2H_5)_2O$ is present than when H_2SO_4 is used, and the yields of the glycerol chloro ethers are higher: 77.5% of the methyl ether and 71% of the ethyl ether. These ethers were then converted into the respective glycidol ethers by the use of a solid caustic alkali (in absolute ether).

1. Reaction of glycidol methyl ether with acetamide. 3.6 g of acetamide, 6.5 g of the ether (20% excess), and 3 drops of the catalyst – conc. NaOH – were heated together in a sealed tube to 140-150° on an oil bath for 10 hours. The reaction mixture was chilled to -10° to precipitate the unreacted acetamide. The precipitated amide was filtered out, and then the reaction product was processed three times with absolute ether, using 25 ml at a time, which threw down a little more of the amide. A total of 1.04 g (30%) of the acetamide was thus recovered unchanged. After the ether had been driven off on a water bath, the reaction product was twice fractionated in vacuo, yielding 3.9 g (36%) of N-propanol-2-methoxy-3-acetamide, 2.9 g (33.7%) of N,N-di-(propanol-2-methoxy-3)--acetamide, and 2.8 g of a polymer.

Experiments run under similar conditions with toluene or at a somewhat

higher temperature (165° instead of 140-150°) manifested no advantages. It should be added that acetamide did not react with glycidol ethers at all when the NaOH catalyst was absent.

The resultant products – the N-mono and N,N-disubstitution derivatives of acetamide – are oily, light-yellow liquids with a faint specific odor, freely soluble in alcohol, acetone, and ether.

Analysis of N-propanol-2-methoxy-3-acetamide.

0.1112 g subs.: 7.54 ml 0.1 N H_2SO_4 (Kjeldahl method); 0.1358 g subs.: 9.26 ml 0.1 N. H_2SO_4; 0.1494 g subs.: 0.2354 g AgI (Zeisel method). Found %: N 9.49, 9.47; CH_3O 20.79. $C_6H_{13}O_3N$. Calc. %: N 9.52; CH_3O 21.07.

Determination of the number of hydroxyl groups. A weighed sample was heated on a boiling water bath for 4 hours with a titrated mixture of acetic anhydride and pyridine (10%), the excess acetic acid being back-titrated with a 0.1N solution of alkali after the reaction mixture had been poured into water.

0.1204 g subs.: 8.14 ml 0.1 N NaOH; 0.1314 g subs.: 8.68 ml 0.1 N. NaOH. Found %: OH 11.49, 11.22. $C_6H_{12}O_2(OH)N$. Calc. %: OH 11.56.

Analysis of N,N-di-(propanol-2-methoxy-3)-acetamide.

0.1107 g subs.: 4.58 ml 0.1 N H_2SO_4 (Kjeldahl method); 0.1169 g subs.: 4.75 ml 0.1 N H_2SO_4; 0.1192 g subs.: 0.2474 g AgI (Zeisel method); 0.1154 g subs.: 9.63 ml 0.1 N NaOH; 0.1203 g subs.: 9.98 ml 0.1 N. NaOH. Found %: N. 5.80, 5.68; CH_3O 27.38; OH 14.18 14.10. $C_{10}H_{19}O_3N(OH)_2$. Calc. %: N. 5.95; CH_3O 27.23; OH 14.46.

In addition to the N-mono and N,N-disubstitution derivatives of acetamide, the high-boiling fraction yielded a small quantity of a thick, oily liquid with the following constants:

B.p. 200-211° at 6 mm; d_4^{15} 1.094; n_D^{15} 1.4460.

0.1460 g subs.: 4.18 ml 0.1 N H_2SO_4 (Kjeldahl method). Found %: N 4.01. $C_{18}H_{37}O_8N$. Calc. %: N 3.49.

To judge from the analytical data, this substance apparently is a product of the reaction of the N,N-disubstitution derivative of acetamide with two more molecules of the ether. The product was not analyzed further.

2. Reaction of glycidol ethyl ether with acetamide. The reaction of 7.15 g (0.07 mol) of the ethyl ether with 3 g (0.05 mol) of acetamide in the presence of 1-3 drops of NaOH under the conditions specified above yielded 3.2 g (26.4%) of N-propanol-2-ethoxy-3-acetamide, 1 g (10%) of N,N-di-(propanol-2-ethoxy-3)--acetamide, a fraction with a b.p. of 220-230° at 6 mm, and 1.5 g of a polymer. As in the experiments with the glycidol methyl ether, 20 to 30% of the unreacted acetamide was recovered.

Analysis of N-propanol-2-ethoxy-3-acetamide.

0.1198 g subs.: 7.45 ml 0.1 N H_2SO_4 (Kjeldahl method); 0.1234 g subs.: 7.58 ml 0.1 N. H_2SO_4; 0.1168 g subs.: 0.1717 g AgI (Zeisel method); 0.1246 g subs.: 7.61 ml 0.1 N NaOH; 0.1188 g subs.: 7.20 ml 0.1 N NaOH. Found %: N 8.70, 8.60; C_2H_5O 28.23; OH 10.38, 10.30. $C_7H_{14}O_2N(OH)$. Calc. %: N 8.69; C_2H_5O 27.92; OH 10.55.

Analysis of N,N-di-(propanol-2-ethoxy-3)-acetamide.

0.1258 g subs.: 4.32 mg 0.1 N H_2SO_4 (Kjeldahl method); 0.1125 g subs.: 3.82 ml 0.1 N H_2SO_4; 0.0738 g subs.: 0.2971 g AgI (Zeisel method); 0.1145 g subs.: 7.95 ml 0.1 N. NaOH; 0.1056 g subs.; 7.21 ml 0.1 N. NaOH. Found %: N 4.80, 4.75; C_2H_5O 32.84; OH 11.80, 11.60. $C_{12}H_{23}O_3(OH)_2N$. Calc. %: N 5.32; C_2H_5O 34.19; OH 12.91.

Analysis of the fraction with a b.p. of 220-230° at 6 mm: d_4^{20} 1.0697; n_D^{20} 1.4620; MR_D 120.10; Calc. 120.42.

0.1559 g subs.: 3.48 ml 0.1 N. H_2SO_4 (Kjeldahl method). Found %: N 3.12. $C_{22}H_{45}O_9N$. Calc. %: N 2.99.

As far as can be judged from the data cited, the synthesized substance apparently is a condensation product of a N,N-disubstitution derivative of acetamide with two more molecules of the glycidol ether. The product was a thick, oily liquid with a specific acrid odor. The substance was not investigated any further.

3. Reaction of glycidol methyl ether with ethanesulfonamide. The reaction of 5.6 g of ethanesulfonamide (m.p. 58°) with 9.0 g (2 mols) of glycidol methyl ether in the presence of 4 drops of conc. NaOH under the conditions specified above yielded 1.5 g of the N-mono and 1 g of the N,N-disubstitution derivatives of ethanesulfonamide, to judge from the nitrogen analysis data.

Analysis of N-propanol-2-methoxy-3-ethanesulfonamide.

0.1202 g subs.: 5.99 ml 0.1 N. H_2SO_4 (Kjeldahl method); 0.1532 g subs.: 7.80 ml 0.1 N. H_2SO_4. Found %: N 6.97, 7.12. $C_5H_{15}SNO_4$. Calc. %: N 7.10.

Analysis of N,N-di-(propanol-2-methoxy-3)-ethanesulfonamide.

0.1490 g subs.: 5.70 ml 0.1 N H_2SO_4 (Kjeldahl method). Found %: N 5.35. $C_{10}H_{23}SNO_8$. Calc. %: N 4.91.

The synthesized N-mono and N,N-disubstitution derivatives of ethanesulfonamide are yellow-brown oils with a faint odor, which are freely soluble in alcohol and acetone. When fractionated in vacuum, the products begin to decompose in the distilling flask at 127° (4 mm). The substances were not analyzed further owing to the small quantities synthesized.

Experiments were also run under similar conditions on the reaction of glycidol ethyl ether with ethanesulfonamide. We also secured a product that was freely soluble in alcohol and acetone (sparingly soluble in petroleum ether). Repeated efforts to isolate it in the pure state and identify it were unsuccessful. Nor did we manage to isolate or identify the reaction products formed when the glycidol methyl and ethyl ethers were reacted with benzenesulfonamide under the conditions described.

SUMMARY

1. A study has been made of the reactions of the glycidol methyl and ethyl ethers with acetamide, ethanesulfonamide, and benzenesulfonamide.

2. The following products of these reactions: N-propanol-2-methoxy-3--acetamide, N,N-di-(propanol-2-methoxy-3)-acetamide, N-propanol-2-ethoxy-3--acetamide, and N,N-di-(propanol-2-ethoxy-3)-acetamide, have been isolated and identified.

3. It has been shown that it is much more difficult for the glycidol ethers to react with ethane- and benzenesulfonamides than with acetamide.

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THE SYNTHESIS OF SOME AMINOGUANIDINE DERIVATIVES

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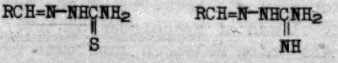
A report [1] was published in the literature at the end of 1946 on the anti-tuberculosis activity *in vitro* of some thiosemicarbazones. Several papers were published in 1947-1949 [2, 3, 4], dealing with investigations of a large number of thiosemicarbazones in experiments *in vivo*. According to the authors of these papers, the most active of these, p-acetaminobenzalthiosemicarbazone (the preparation Domagk Tb I 698) has been tested clinically and has been employed in treating some forms of tuberculosis.

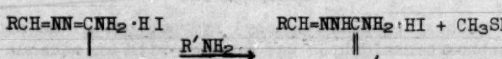
We were interested in making a study of the antituberculosis activity of carbonyl derivatives of aminoguanidine. Structurally, the latter may be regarded as thiosemicarbazones in which the sulfur has been replaced by an amino group:



We synthesized the aminoguanyl derivatives of benzaldehyde, vanillin, and p-acetaminobenzaldehyde, as well as their N-butyl and N-octyl derivatives. The aminoguanidine required for synthesizing the aminoguanyl derivatives was prepared as its hydrochloride by reacting methylisothiourea with hydrazine sulfate [5]. The aminoguanyl derivatives of the foregoing aldehydes were synthesized by condensing aminoguanidine with aldehydes

The N-alkyl derivatives of the aminoguanyls were synthesized in two ways.

1. Reacting the hydriodides of S-methylthiosemicarbazones with alkyl amines:

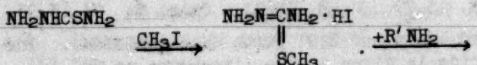


It was found that an alkyl amino group is substituted for the methylmercapto group in methylthiosemicarbazones when the constituents are boiled in alcohol for a long time. The lengthy heating causes partial tarring, which interferes with the isolation of the substance in the pure state.

2. Reacting an N-alkyl aminoguanidine with a carbonyl compound:

(IV)

The N-alkyl aminoguanidines were synthesized as follows [6]:



(I) (II)

$$\longrightarrow \quad NH_2NHCNH_2 \cdot HI \quad + CH_3SH \ .$$
$$\quad\quad\quad

3-Hydroxy-4-methoxybenzal-N^4-butylaminoguanyl hydrochloride. a) 1 g of 3-hydroxy-4-methoxy-benzal-5-methylisothisosemicarbazone was boiled for 18 hours in 10 ml of absolute alcohol with 22 g of n-butylamine. The alcohol was evaporated in vacuo, and the residual oil was triturated with dilute hydrochloric acid. The resulting brown crystals were refined by repeated recrystallization from alcohol containing activated charcoal. M.p. 198-199°.

b) 2 g of thiosemicarbazide and 3.14 g of methyl iodide were heated in 15 ml of absolute alcohol until all the thiosemicarbazide dissolved, and 1.6 g of n-butylamine was added to the resulting alcoholic solution of 5-methylisothisosemicarbazide hydriodide. The solution was boiled for 30 minutes. Then the alcohol was evaporated in vacuo, and the remaining N-butylaminoguanidine, a thick oil, was treated with a solution of 3.25 g of vanillin in 10 ml of alcohol and a few drops of hydrochloric acid. The mixture was boiled for an hour, the alcohol driven off in vacuo, and the oil thoroughly triturated with dilute hydrochloric acid. The yellowish precipitate was recrystallized twice from alcohol. M.p. 200-201°. The product was the same as that prepared by the previous method.*

p-Acetaminobenzal-N^4-butylaminoguanyl hydriodide. 1 g of thiosemicarbazide, 1.57 g of methyl iodide, 0.85 g of n-butylamine, and 1.79 g of p-acetaminobenzaldehyde were processed in the same sequence of operations as that described in Test (b) for the N^4-butylaminoguanyl derivative of vanillin. The crystals secured after repeatedly treating the oily reaction product with hydrochloric acid were not the expected hydrochloride, but p-acetaminobenzaldehyde-N^4-butylaminoguanyl hydriodide. The latter was purified by recrystallization from water with activated charcoal; a light-yellow substance with a m.p. of 223-225°.

3.294 mg subs.: 0.516 ml N_2 (29°, 721 mm). Found %: N 16.78. $C_{14}H_{22}N_5OI$. Calc. %: N 17.23.

Benzal-N^4-butylaminoguanyl hydrochloride. These snow-white crystals were secured after double recrystallization from a small amount of alcohol. M.p. 210.5-212°.

3.926 mg subs.: 0.784 ml N_2 (26.5°, 724 mm). Found %: N 21.67. $C_{12}H_{18}N_4Cl$. Calc. %: N 21.97.

Benzal-N^4-octylaminoguanyl hydrochloride. These snow-white crystals were secured from alcohol containing ether. M.p. 176-177°.

3.000 mg subs.: 7.544 mg CO_2; 2.560 mg H_2O; 3.141 mg subs.: 0.526 ml N_2 (30.0°, 724 mm). Found %: C 62.43; H 8.68; N 17.94. $C_{16}H_{27}N_4Cl$. Calc. %: C 61.99; H 8.69; N 18.03.

p-Acetaminobenzal-N^4-octylaminoguanyl hydrochloride. This was synthesized as yellow crystals by recrystallization from water containing activated charcoal, followed by recrystallization from alcohol. M.p. 211-213°. Freely soluble in alcohol and acetone, less so in water, and insoluble in ether.

3.195 mg subs.: 0.537 ml N_2 (22°, 730 mm); 3.225 mg subs.: 0.544 ml N_2 (22°, 732 mm). Found %: N 18.70, 18.93. $C_{18}H_{30}ON_5Cl$. Calc. %: N 19.03.

SUMMARY

Several benzalguanyl substitution derivatives and their N^4-alkyl derivatives have been synthesized. These compounds possess antituberculosis activity, but are toxic.

* 3.752 mg subs.: 7.188 mg CO_2; 2.339 mg H_2O; 3.426 mg subs.: 6.548 mg CO_2; 2.090 mg H_2O; 3.301 mg subs.: 0.577 ml N_2 (29.5°, 720.5 mm); 5.300 mg subs.: 2.618 mg AgCl. Found %: C 52.32, 52.12; H 6.97, 6.82; N 18.69; Cl 12.22. $C_{13}H_{21}N_4O_2Cl$. Computed %: C 51.95; H 6.98; N 18.63; Cl 11.83.

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MIXED SULFIDES WITH C_{11} – C_{20} CARBON ATOMS AND THEIR FUNDAMENTAL CONSTANTS

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We are the first to have synthesized the hitherto undescribed mixed sulfides whose synthesis and constants are set forth in this report.

These sulfides have been produced by the general method first proposed by F. Kruger [1] for synthesizing mixed sulfides, viz.: reacting metallic derivatives of the thiols with the appropriate halides as follows:

$$R\text{–}S\text{–}Me + R_1Hal \rightarrow R\text{–}S\text{–}R_1 + MeHal.$$

The usual procedure employed to synthesize these sulfides was as follows: equimolecular quantities of the thiol, a caustic alkali (caustic potash or soda), and an alkyl halide were used. The apparatus in which the synthesis was carried out consisted of a round-bottomed flask fitted with a dropping funnel and a reflux condenser. The caustic alkali was dissolved by heating it on a water bath with 1.5-2 mols of ethyl alcohol or methanol. Then the thiol was added a drop at a time to the alcoholic solution of the alkali without interrupting the heating. When all the thiol had been added, the reaction mass was heated to 60-70 for 30 minutes. Then the alkyl halide was added drop by drop, the bath being kept at that same temperature. This usually caused a white precipitate of the metal halide to settle out at once. When all the alkyl halide had been added, the heating of the reaction mixture to 60-70° was continued for another 1.5-2 hours. The sulfide settled out as an oily layer. After the mixture had cooled, water was added to the flask, causing the metal halide to dissolve. The sulfide was extracted with ether, the ether extract being washed with a 10% alkali solution to eliminate the unreacted thiol and with water until its reaction was neutral, after which it was dried with calcium chloride. The ether was then driven off, and the synthesized sulfide fractionated in vacuo.

In calculating the molar refractions we took the atomic refraction of sulfidic sulfur to be 7.97, in conformity with the findings of T. S. Price and D. F. Twiss [2]. The parallel determinations of carbon, hydrogen, and sulfur were made by the procedure elaborated by M. O. Korshun and his associates [3,4].

1. Phenyl decyl sulfide was produced by reacting potassium thiophenolate with decyl bromide. The yield was 84.4% of the theoretical.

The thiophenol was prepared by the method described in Syntheses of organic preparations [5] and had the following constants: b.p. 68 (22 mm); n_D^{20} 1.5888; d_4^{20} 1.0780. The figures given in the literature are: b.p. 77 (30 mm); $n_D^{23.2}$ 1.58613; $d_4^{23.2}$ 1.0739[6].

The decyl bromide was prepared from decyl alcohol by reacting it with bromine and phosphorus; it had a b.p. of 97-98° (5 mm); n_D^{20} 1.4550; d_4^{20} 1.0689.

Figures in the literature: b.p. 104-104.5° (8 mm); n_D^{20} 1.4550; d_4^{20} 1.0683 [7].

Constants of phenyl decyl sulfide: b.p. 170-171° (5 mm); m.p. 21°; n_D^{24} 1.5213; d_4^{24} 0.9341; MR_D 81.47; Calc. 80.46.

3.775 mg subs.: 10.620 mg CO_2; 3.420 mg H_2O. 3.920 mg subs.: 10.800 mg CO_2; 3.600 mg H_2O. Found %: C 76.84, 76.89; H 10.15, 10.28. $C_{16}H_{26}S$. Calc. %: C 76.8; H 10.4.

2. Phenyl cyclopentyl sulfide was synthesized from potassium thiophenolate and cyclopentyl bromide, the yield being 65%.

The cyclopentyl bromide, prepared by saturating cyclopentanol with gaseous hydrogen bromide [8], had a b.p. of 135° (746 mm); n_D^{20} 1.4890; d_4^{20} 1.3863.

The figures given in the literature for cyclopentyl bromide: b.p. 136-138°; d^4 1.370 [8]; b.p. 136-138°; d^8 1.380 [10]; b.p. 137-139°; n_D^{18} 1.4875; d_{18}^{18} 1.400 [11].

Constants of phenyl cyclopentyl sulfide: b.p. 139.5° (13 mm); n_D^{20} 1.5740; d_4^{20} 1.0571; MR_D 55.62; Calc. 55.17.

5.040 mg subs.: 13.645 mg CO_2; 3.525 mg H_2O. 5.390 mg subs.: 14.645 mg CO_2; 3.765 mg H_2O. Found %: C 73.98, 74.15; H 7.82, 7.89. $C_{11}H_{14}S$. Calc. %: C 74.08; H 7.92.

3. Cyclohexyl decyl sulfide was synthesized by reacting a sodium derivative of cyclopentanol with decyl bromide, the yield being 62%.

Cyclohexanethiol was prepared by reacting cyclohexylmagnesium bromide with sulfur [12]. Constants of cyclohexanethiol: b.p. 90-91° (100 mm); n_D^{20} 1.4911; d_4^{20} 0.9584.

Figures in the literature for cyclohexanethiol: b.p. 90° (100 mm); n_D^{20} 1.4933; d_4^{20} 0.9486 [13].

Constants of cyclohexyl decyl sulfide: b.p. 164-165° (2 mm); n_D^{20} 1.4820; d_4^{20} 0.8846; MR_D 82.48; Calc. 81.86.

6.000 mg subs.: 16.520 mg CO_2; 6.818 mg H_2O. 3.960 mg subs.: 10.885 mg CO_2; 4.450 mg H_2O. 5.990 mg subs.: 2.270 mg SO_4. 6.460 mg subs.: 2.450 mg SO_4. Found %: C 75.14; 75.02; H 12.71, 12.57. S 12.65, 12.66. $C_{16}H_{32}S$. Calc. %: C 75.0; H 12.5; S 12.5.

An attempt to synthesize cyclohexyl decyl sulfide by reacting cyclohexyl bromide with sodium decyl mercaptide was less successful. The sulfide yield was 17%, due to a side reaction in which the influence of the alkali caused the formation of cyclohexene from the cyclohexyl bromide.

4. Cyclopentyl decyl sulfide was synthesized by reacting the potassium mercaptide of cyclopentanethiol with decyl bromide.

Cyclopentanethiol was prepared by reacting potassium hydrosulfide with cyclopentyl bromide [14]. The constants of the cyclopentanethiol were: b.p. 130° (746 mm); n_D^{20} 1.4882; d_4^{20} 0.9485. The literature gives the b.p. of cyclopentanethiol as 131.5-132° [14], no other constants being cited.

Cyclopentyl decyl sulfide was synthesized in the usual manner. The yield was 72% of the theoretical.

B.p. 158° (2 mm); n_D^{20} 1.4786; d_4^{20} 0.8833; MR_D 77.72; Calc. 77.24.

6.060 mg subs.: 16.505 mg CO_2; 6.800 mg H_2O. 2.410 mg SO_4. 6.480 mg subs.: 17.625 mg CO_2; 7.230 mg H_2O; 3.220 mg SO_4. Found %: C 74.35, 74.25; H 12.55, 12.49; S 13.28, 13.18. $C_{15}H_{30}S$. Calc. %: C 74.29; H 12.48; S 13.23.

5. Cyclohexyl cyclopentyl sulfide was synthesized by reacting the potassium mercaptide of cyclohexanethiol with cyclopentyl bromide. The yield was 67% of the theoretical.

B.p. 119-120° (3 mm); n_D^{20} 1.5118; d_4^{20} 0.9692; MR_D 56.90; Calc. 56.57.

6.290 mg subs.: 16.520 mg CO_2; 6.250 mg H_2O; 3.270 mg SO_4. 5.100 mg subs.: 13.370 mg CO_2; 5.080 mg H_2O; 2.650 mg SO_4. Found %: C 71.67, 71.56; H 11.12, 11.15; S 17.35, 17.34. $C_{11}H_{20}S$. Calc. %: C 71.73; H 10.87; S 17.38.

6. α-Naphthyl decyl sulfide was synthesized from potassium α-thionaphtholate and decyl bromide.

The α-thionaphthol was prepared by reducing α-naphthalene monosulfonic chloride with zinc dust and hydrochloric acid [15]. The constants of the resultant α-thionaphthol were: b.p. 142-142.5° (7 mm); n_D^{20} 1.6802; d_4^{20} 1.1607.

Figures in the literature for α-thionaphthol: b.p. 144.8° (10.3 mm) [15]; b.p. 152.5-153.5° (15 mm); d_4^{20} 1.1549 [16].

In synthesizing α-naphthyl decyl sulfide we departed from the standard procedure by heating the reaction mixture on a glycerol bath at 120-130° instead of carrying it out at 60-70° as is customary. This was done because F. Kraft and R. Schonherr [16], who synthesized α-naphthyl ethyl sulfide, recommend that the reaction be carried out at higher temperatures when α-thionaphthol is used. The yield of α-naphthyl decyl sulfide was 72% of the theoretical.

B.p. 234-235° (7-8 mm); n_D^{20} 1.5714; d_4^{20} 0.9893; MR_D 99.64; Calc. 95.80.

4.800 mg subs.: 14.060 mg CO_2; 4.090 mg H_2O; 1.535 mg SO_4. 4.980 mg subs.: 14.585 mg CO_2; 4.240 mg H_2O; 1.595 mg SO_4. Found %: C 79.94, 79.92; H 9.54, 9.53; S 10.67, 10.89. $C_{20}H_{28}S$. Calc. %: C 80.0; H 9.33; S 10.66.

7. α-Naphthyl cyclohexyl sulfide was synthesized from sodium α-thionaphtholate and cyclohexyl bromide.

The cyclohexyl bromide was synthesized by saturating cyclohexanol with gaseous hydrogen bromide [17]. The constants of the synthesized cyclohexyl bromide were: b.p. 163-164° (760 mm); n_D^{20} 1.4950; d_4^{20} 1.3357.

Figures in the literature: b.p. 163-165.5°; d_0^0 1.3604 [18]; b.p. 163-166.5° (760 mm); $n_D^{14.6}$ 1.49564; $d_4^{14.6}$ 1.3264 [19].

The conditions employed in synthesizing α-naphthyl cyclohexyl sulfide were the same as those used in synthesizing the preceding preparation, i.e., heating on a glycerine bath to 120°. The yield of α-naphthyl cyclohexyl sulfide was 31.4% of the theoretical. This low yield was due to a side reaction in which cyclonexene was formed, 35% of the initial cyclohexyl bromide being converted into cyclohexene.

The constants of the synthesized α-naphthyl cyclohexyl sulfide were: b.p. 201-202° (7 mm); n_D^{20} 1.6306; d_4^{20} 1.0953; MR_D 78.64; Calc. 75.12.

5.650 mg subs.: 16.435 mg CO_2; 3.740 mg H_2O; 2.230 mg SO_4. 6.030 mg subs.: 17.535 mg CO_2; 4.070 mg H_2O; 2.400 mg SO_4. Found %: C 79.39, 79.36; H 7.47, 7.55; S 13.18, 13.28. $C_{16}H_{18}S$. Calc. %: C 79.34; H 7.43; S 13.22.

8. β-Tetralyl cyclohexyl sulfide was synthesized from the sodium derivative of β-thiotetralol and cyclohexyl chloride.

The β-thiotetralol was prepared by reducing β-tetralin sulfochloride with zinc dust and hydrochloric acid [20].

Constants of β-thiotetralol: b.p. 151-151.5° (15 mm); n_D^{20} 1.5972; d_4^{20} 1.0884.

Figures in the literature: b.p. 146-148° (14 mm) [20].

The cyclohexyl chloride (a ready preparation) had a b.p. of 141.5-142.5° (749 mm); n_D^{20} 1.4610; d_4^{20} 1.0030. The figures given in the literature for cyclohexyl chloride are: b.p. 141° (760 mm); n_D^{20} 1.46264; d_4^{20} 1.0000 [9].

The β-tetralyl cyclohexyl sulfide was synthesized by heating the reaction mixture to 120° on a glycerin bath. The yield was 34.9% of the theoretical. The low sulfide yield is attributable to a side reaction in which the alcoholic alkali converted the cyclohexyl chloride into cyclohexene

Attempts to synthesize the tetralyl cyclohexyl sulfide from cyclohexyl bromide produced an even lower yield of the sulfide. Lowering the reaction temperature likewise lowered the yield.

Constants of the synthesized β-tetralyl cyclohexyl sulfide: b.p. 187.5-188.5° (3 mm); n_D^{20} 1.5800; d_4^{20} 1.0543; MR_D 77.65; Calc. 75.92.

5.735 mg subs.: 16.450 mg CO_2; 4.580 mg H_2O; 2.240 mg SO_4. 6.090 mg subs.: 17.425 mg CO_2; 4.875 mg H_2O; 2.360 mg SO_4. Found %: C 78.28, 78.11; H 8.95, 8.96; S 13.03, 12.94. $C_{16}H_{22}S$. Calc. %: C 77.99; H 9.00; S 13.01.

SUMMARY

The following mixed sulfides have been synthesized and described for the first time by reacting aliphatic and naphthenic halogen derivatives with metallic derivatives of aliphatic, aromatic, and naphthenic thiols: phenyl decyl sulfide, phenyl cyclopentyl sulfide, cyclohexyl decyl sulfide, cyclopentyldecyl sulfide, cyclohexyl cyclopentyl sulfide, α-naphthyl decyl sulfide, α-naphthyl cyclohexyl sulfide, and β-tetralyl cyclohexyl sulfide.

The yields were satisfactory (ranging from 62 to 84%) except when the halide used was a cyclohexyl halide. Then the yields dropped to 30-34% owing to a side reaction in which cyclohexene was formed.

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SYNTHESIS OF THE DISACCHARIDES

VI. SYNTHESIS OF GLUCOSIDO-2-GALACTOSE

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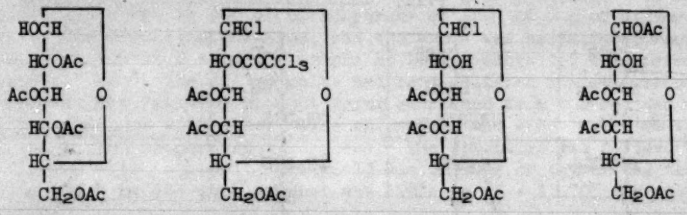
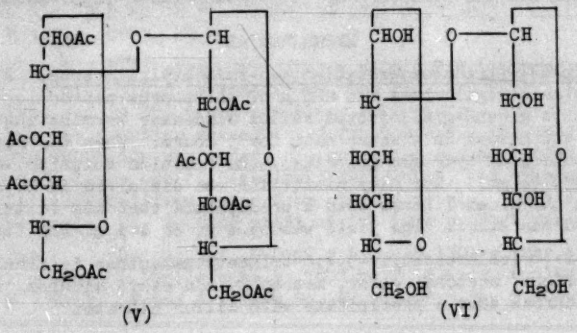
In our previous research the following disaccharides have been synthesized: glucosido-2-glucose [1], galactosido-2-galactose [2], galactosido-2-glucose [3], glucosido-3-glucose, and galactosido-3-glucose [5]. In the present paper we shall describe the synthesis of glucosido-2-galactose.

The initial substances used in this synthesis were 2,3,4,6-tetraacetylglucose (I) and 1,3,4,6-tetraacetylgalactose (IV). β-2,3,4,6-Tetraacetylglucose was synthesized from glucose via the pentaacetate and acetobromoglucose [6]. The 1,3,4,6-tetraacetylgalactose was synthesized from pentaacetylgalactose [7], which was converted by the action of phosphorus pentachloride into 1-chloro-2-(trichloroacetyl)-3,4,6-triacetylgalactose (II), saponification of the latter compound with ammonia in ether solution readily yielding 1-chloro-3,4,6-triacetylgalactose (III). Reacting 1-chloro-3,4,6-triacetylgalactose with silver acetate yielded 1,3,4,6-tetraacetylgalactose (IV).



(I) (II) (III) (IV)

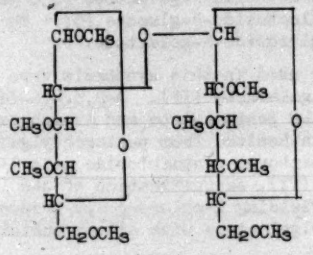
Condensing β-2,3,4,6-tetraacetylglucose with 1,3,4,6-tetraacetylgalactose yielded the octaacetate of glucosido-2-galactose (V), which was converted into glucosido-2-galactose (VI).



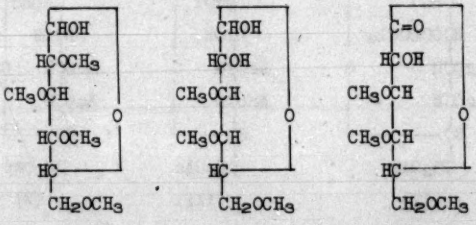
(V) (VI)

The disaccharide was identified as its hydrazone and its bionic acid. It reduces Fehling's solution. Splitting a hydrogen atom from the reducing part of the disaccharide yielded glucosidopentose, which does not reduce Fehling's solution or react with phenylhydrazine.

The positions of the oxygen bridges were determined by methylation, hydrolysis and oxidation. Hydrolysis of the completely methylated disaccharide (VII) yielded 2,3,4,6-tetramethylglucose (VIII) and 3,4,6-trimethylgalactose (IX). 2,3,4,6-Tetramethylglucose was identified as its anilide, and the 3,4,6-trimethylgalactose via its δ-lactone (X). The production of 2,3,4,6-tetramethylglucose and of the δ-lactone is evidence of the pyranose structure of the two monoses comprising the disaccharide we had synthesized.



(VII)



(VIII) (IX) (X)

These findings, plus the course of the synthesis itself, indicate that the disaccharide has the structure of (1,5)-glucosido-2-(1,5)-galactose (VI).

EXPERIMENTAL

1. 1-Chloro-2-(trichloroacetyl)-3,4,6-triacetylgalactose. A mixture of 117.0 g of pentaacetylgalactose and 200 g of phosphorus pentachloride was placed in a flask with a ground-glass-fitted reflux condenser terminating in a calcium chloride tube and heated on a water bath for 3 hours. When the reaction was over (test for evolution of hydrogen chloride), the reaction solution was distilled at reduced pressure (2 mm). The oily distillate was dissolved in 10 ml of amyl alcohol; chilling the alcohol threw down a precipitate that was filtered out and washed with cold anhydrous ether. The yield was 63.1 g, or 46% of the theoretical.

1-Chloro-2-(trichloroacetyl)-3,4,6-triacetylgalactose is freely soluble in benzene, chloroform, acetone, ether, methanol, and ethyl alcohol, reduces Fehling's solution, and throws down a precipitate with silver nitrate.

The melting point of the pure product was 150-156°; α_D^{20} 10.4° (in benzene, C = 2.71). 0.0964 g subs.: 0.1194 g AgCl. Found %: Cl 30.61. $C_{14}H_{16}O_8Cl_4$. Calc. %: Cl 30.21.

2. 1-Chloro-3,4,6-triacetylgalactose. 58 g of 1-chloro-2-(trichloroacetyl)-3,4,6-triacetylgalactose was dissolved in 400 ml of anhydrous ether that had been saturated with anhydrous ammonia at 0°. Then the reaction solution was kept at room temperature for 3 hours and chilled strongly, causing the precipitation of flocs of the ammonium salt. The solution was filtered and then evaporated to dryness, the 1-chloro-3,4,6-triacetylgalactose being extracted from the residue with ethyl acetate. After the ethyl acetate had been driven off, the resultant crystals were recrystallized from ethyl alcohol. The yield was 23.7 g, or 59% of the theoretical.

M.p. 159-167°; α_D^{20} + 29.10° (in ethyl acetate, C = 3.40).

1-Chloro-3,4,6-triacetylgalactose is freely soluble in ether, acetone, chloroform, and ethyl alcohol.

0.1013 g subs.: 0.0435 g AgCl; 0.1519 g subs.: 0.0666 g AgCl. Found %: Cl 10.64, 10.77. $C_{12}H_{17}O_8Cl$. Calc. %: Cl 10.94.

The 1-chloro-3,4,6-triacetylgalactose was also identified via α-tetraacetylgalactose [m.p. 95-96°; α_D^{20} + 106° (in chloroform)] and 1,2-dichloro-3,4,6-triacetylgalactose [m.p. 99-101°; α_D^{20} + 37.4° (in ethyl alcohol)].

3. 1,3,4,6-Tetraacetylgalactose. 16.2 g of 1-chloro-3,4,6-triacetylgalactose was dissolved in 300 ml of anhydrous ether. 16.6 g of silver acetate was added to the resulting solution, and the whole was agitated at room temperature for 2 hours (until a solution sample no longer exhibited the presence of any halogens). After the silver salts had been filtered out, the ether was evaporated to dryness, the reaction product being extracted from the residue with chloroform at first and then with ether. The chloroform and ether extracts were combined, desiccated, and evaporated to dryness. The substance was refined by recrystallizing it from ethyl alcohol. The yield was 12.9 g, or 74% of the theoretical. The melting point of the pure product was 128°; α_D^{20} + 11.70° (in ethyl alcohol, C = 2.00).

1,3,4,6-Tetraacetylgalactose is freely soluble in chloroform, ether, acetone, ethyl alcohol, and pyridine.

0.1234 g subs.: 0.2197 g CO_2; 0.0781 g H_2O; 0.0849 g subs.: 0.1564 g CO_2; 0.0488 g H_2O; 0.1810 g subs.: 21.2 ml 0.1 N NaOH. Found %: C 48.15, 48.52; H 6.40, 6.31; $COCH_3$ 49.17. $C_{14}H_{20}O_{10}$. Calc. %: C 48.28; H 5.71; $COCH_3$ 49.40.

4. Condensing 2,3,4,6-tetraacetylglucose with 1,3,4,6-tetraacetylgalactose. A mixture of 12.5 g of 2,3,4,6-tetraacetylglucose and 12.5 g of 1,3,4,6-tetraacetylgalactose was dissolved in 350 ml of anhydrous chloroform. 6 g of fused zinc chloride was added, and the solution was agitated for 5 hours. The solution was filtered, 15 g of phosphoric anhydride was added, and agitation was continued. Five hours later the chloroform layer was filtered out, desiccated, and evaporated to dryness, the residue being recrystallized twice from ethyl alcohol. The yield was 22 g, or 81% of the theoretical. The melting point of the pure product was 179°.

0.1181 g subs.: 0.1841 g CO_2; 0.0567 g H_2O. 0.1701 g subs.: 0.2634 g CO_2, 0.0871 g H_2O; 0.1561 g subs.: 18.7 ml 0.1N Na OH; 0.2107 g subs.: 25 ml 0.1 N NaOH. Found %: C 48.95, 49.26; H 5.34, 5.70; $COCH_3$ 50.52,

50.39. $C_{28}H_{38}O_{19}$. Calc. %: C 49.56; H 5.60; $COCH_3$ 50.64.

5. β-(1,5)-Glucosido-2-(1,5)-galactose. 20 g of β-(1,5)-glucosido-2-(1,5)-galactose octaacetate was dissolved in 150 ml of anhydrous chloroform, the solution was chilled, and 0.7 g of sodium dissolved in 100 ml of absolute methanol was added. The reaction mixture was agitated for 2 hours, a syrupy substance gradually settling out of the solution; then 50 ml of water was added, and agitation was continued. The mixture was neutralized with dilute acetic acid, and the chloroform layer was separated from the aqueous-alcoholic layer, which was evaporated in vacuo to a thick syrup. The residue was stirred with 300 ml of methanol and 200 ml of acetone. The solution was filtered 15 minutes later and then evaporated to dryness. The residual substance was dissolved in the minimum quantity of water and mixed with 40 ml of glacial acetic acid, which threw crystals of the disaccharide down from the solution. The yield was 7 g, or 81% of the theoretical:

M.p. 171-172°; l = 0.5; C = 0.3; α + 6.4°; α_D^{20} + 42.6° (in water).

0.5101 g subs.: 0.7121 g CO_2; 0.2581 g H_2O; 0.6034 g subs.: 0.9242 g CO_2; 0.3601 g H_2O. Found %: C 42.60, 42.78; H 5.82, 6.33. $C_{12}H_{22}O_{11}$. Calc. %: C 42.11; H 6.43.

The melting point of the glucosido-2-galactose phenylhydrazone was 181°.

0.1134 g subs.: 5.9 ml N_2 (15°, 732 mm); 0.1891 g subs.: 9.9 ml N_2 (15°, 732 mm). Found %: N 6,13, 5.95. $C_{18}H_{28}O_{10}N_2$. Calc. %: N 6.49.

6. Oxidizing β-(1,5)-glucosido-2-(1,5)-galactose and hydrolysis of the resultant bionic acid. 5 g of β-(1,5)-glucosido-2-(1,5)-galactose was dissolved in 250 ml of bromine water, and the resultant solution was agitated and then exposed to light. Then the solution was neutralized with calcium carbonate, filtered, and evaporated to minimum volume. When absolute ethyl alcohol was slowly added to the thickened solution, flocs of the calcium salt of glucosido-2-galactonic acid settled out. The salt was filtered out and recrystallized from water.

0.0721 g subs.: 0.0056 g CaO; 0.0854 g subs.: 0.0067 g CaO. Found %: Ca 5.68, 5.74. $(C_{12}H_{21}O_{12})_2Ca$. Calc. %: Ca 5.31.

When the calcium salt of glucosido-2-galactonic acid was decomposed with the calculated quantity of oxalic acid and the calcium salts had been filtered out of the solution, the resultant acid was hydrolyzed with a 5% solution of sulfuric acid. The solution was neutralized with calcium carbonate and filtered, the filtrate being evaporated to minimum volume. When absolute ethyl alcohol was slowly added to the thickened solution, flocs of calcium galactonate settled out; the precipitate was filtered out and crystallized from water.

0.1101 g subs.: 0.0145 g CaO. Found %: Ca 9.39. $(C_6H_{11}O_7)_2Ca$. Calc. %: Ca 9.30.

After the calcium galactonate had been filtered out, the filtrate was boiled with phenylhydrazine and acetic acid. As the solution cooled, crystals with a m.p. of 205-207° settled out. The mixed melting point with glucosazone exhibited no depression.

7. Oxidation of the calcium salt of glucosido-2-galactonic acid. 5.5 g of the calcium salt of glucosido-2-galactonic acid was dissolved in 100 ml of water, and 1 g of barium acetate in 100 ml of water and 0.5 g of ferric sulfate in 15 ml of water were added to the solution. The solution was then heated to 70°, and

30 ml of 30% perhydrol was gradually added, with frequent stirring. Then the reaction mixture was allowed to stand at room temperature for 3 hours, with frequent stirring, after which 25 ml more of the perhydrol was added to the solution. The solution warmed up slightly toward the end. The solution was filtered through charcoal and then evaporated to a thick syrup at reduced pressure. The residual glucosido-lycoside did not reduce Fehling's solution nor did it react with phenylhydrazine.

The product crystallized after standing for a long time with glacial acetic acid. The pure product had a m.p. of 139-141°; $\alpha\ D^{20}$ + 5.4° (in water, C = 0.8).

0.1289 g subs.: 0.2013 g CO_2; 0.0812 g H_2O; 0.01 g subs.: 0.1 g camphor: Δt 12.7°; 0.01 g subs.: 0.1 g camphor: Δ t 12.5° Found %: C 42.66; H 7.01; M 316, 319. $C_{11}H_{20}O_{10}$. Calc.: C 42.30; H 6.45; M 312.

The melting point of the acetylated product was 147-149°.

0.1137 g subs.: 13.1 ml 0.1 N. Solution NaOH; 0.1783 g subs.: 20.4 ml 0.1 N. solution NaOH. Found %: $COCH_3$ 49.71, 49.30. $C_{25}H_{34}O_{17}$. Calc. %: $COCH_3$ 49.61.

8. Methylating glucosido-2-galactose. 8.4 g of glucosido-2-galactose was dissolved in 25 ml of water, and dimethyl sulfate and a 25% solution of sodium hydroxide were gradually added to the resulting solution at 40-60°, a total of 40 g of dimethyl sulfate being added. The alkali was added until the reaction of the solution was weakly alkaline. Toward the end the reaction mixture was heated to 100°, and the reaction product was extracted with chloroform. After the chloroform had been evaporated, the remaining syrup was remethylated, this time using 30 g of methyl iodide with 12 g of silver carbonate. The methylated glucosido-2-galactose was extracted with chloroform and distilled in a 2-mm vacuum after the chloroform had been driven off: n_D^{20} 1.4712; $\alpha\ D^{20}$ - 22.7° (in chloroform, C = 0.5). The yield was 15.8 g, or 57% of the theoretical.

0.1001 g subs.: 0.4125 g AgI; 0.1209 g subs.: 0.4927 g AgI. Found %: OCH_3 55.02, 54.72. $C_{20}H_{38}O_{11}$. Calc. %: OCH_3 54.65.

9. Hydrolysis of the methylated disaccharide and identification of the hydrolysis products. 200 ml of a 5% solution of hydrochloric acid was poured over 15 g of octamethylglucosido-2-galactose. The resulting mixture was kept at 80-85° for 1 hour and then boiled for 2 hours. The solution was neutralized with a dilute solution of sodium hydroxide and then evaporated to small volume. The reduced solution was treated five times with 50-ml batches of chloroform. The chloroform extracts were combined, desiccated, and evaporated, resulting in the crystallization of 2,3,4,6-tetramethylglucose with a m.p. of 93-95°; $\alpha\ D^{20}$ + 84.5° (in chloroform, C = 1.2). The yield was 6.0 g. The 2,3,4,6-tetramethylglucose was identified via its anilide with a m.p. of 137-139°; $\alpha\ D^{20}$ + 233.8° (in acetone, C = 2.1).

0.2007 g subs.: 8.4 ml N_2 (16°, 730 mm); 0.2010 g subs.: 8.1 ml N_2 (16°, 730 mm). Found %: N 4.81, 4.59. $C_{18}H_{25}O_5N$. Calc. %: N 4 50.

The solution left after the 2,3,4,6-tetramethylglucose had been extracted with chloroform was evaporated under reduced pressure to dryness. The residual syrup was dissolved in 300 ml of bromine water, the resultant solution being left to stand exposed to light for 3 days, with frequent stirring. Then the solution was thoroughly boiled to eliminate the bromine and neutralized with lead acetate, the excess lead being precipitated out of the filtered solution with hydrogen sulfide, and the solution being again neutralized with calcium carbonate. The

filtrate was evaporated to small volume, the flocs of the calcium salt of 3,4,6-trimethylgalactonic acid settling out when absolute ethyl alcohol was added.

The salt was decomposed with a calculated quantity of oxalic acid, and the filtered solution was evaporated to dryness. The residue was the lactone of 3,4,6-trimethylgalactonic acid. The rapid change of its angle of rotation identified it as the δ-lactone; α_D^{20} + 104.8 → + 24.8° (in water, within 2 minutes).

0.1540 g subs.: 0.2781 g CO_2; 0.1035 g H_2O; 0.1121 g subs.: 0.3556 g AgI. Found %: C 49.19; H 7.51; OCH_3 42.60. $C_9H_{16}O_6$. Calc. %: C 49.09; H 7.28; OCH_3 42.27.

Methylating the lactone of 3.4.6-trimethylgalactonic acid yielded the δ-lactone of 2,3,4,6-tetramethyl-d-galactonic acid, well known in the literature, with a m.p. of 160-161°; α_D^{20} + 144.2° → 25.1° (in water, within 2 minutes). The lactone was identified as its amide, with a m.p. of 119-120°; α_D^{20} + 38.1° (in acetone).

0.1521 g subs.: 6.4. ml N_2 (16°, 730 mm); 0.1910 g subs.: 7.7 ml N_2 (16°, 730 mm). Found %: N 4.78, 4.61. $C_{10}H_{21}O_6N$. Calc. %: N 4.44.

SUMMARY

1. A new disaccharide - glucosido-2-galactose - has been synthesized.

2. Condensing 2,3,4,6-tetraacetylglucose with 1,3,4,6-tetraacetylgalactose in the presence of zinc chloride and phosphoric anhydride yields the octaacetate of glucosido-2-galactose; saponification of the octaacetate yields the disaccharide.

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ISOMERIZATION OF THE DISACCHARIDES

I. IZOMERIZATION OF GLYCOSIDO-3-GLUCOSE

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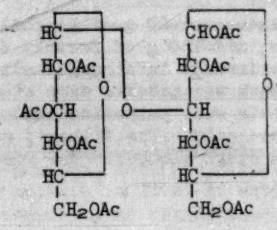
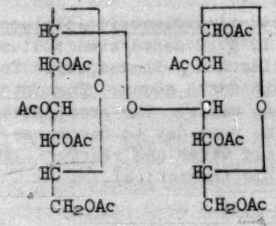
The disaccharides have been synthesized by chemical as well as biochemical methods. The reactions that lead to the conversion of one disaccharide into another may also come under the heading of disaccharide syntheses. A first instance of a reaction of this type is the conversion of cellobiose into glucosido-4-mannose [1]. In his paper Hudson [2] showed that one disaccharide can be converted into another, stereoisomeric, disaccharide by the action of aluminium chloride, the hydroxyl groups and hydrogen atoms exchanging their positions at the 2 and 3 carbon atoms in the reducing part of the disaccharide.

Our research had as its objective the use of askanite for the isomeric conversions of disaccharides. In these tests we employed the disaccharide glucosido-3-glucose [3]. The glucosido-3-glucose was isomerized in organic solvents, so that the disaccharide was first acetylated. The resulting octaacetate of the disaccharide (I) was dissolved in anhydrous chloroform, the solution being mixed with askanite and machine-agitated. The chloroform was filtered and evaporated. The crystals recovered were recrystallized a few times from ethyl alcohol to eliminate the original acetate. As analysis indicated, these crystals were the octaacetate of glucosido-3-mannose (II). Saponifying the octaacetate yielded glucosido-3-mannose (III).



(I)



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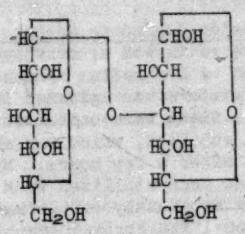
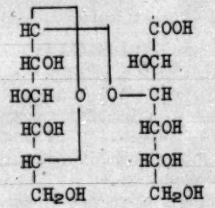
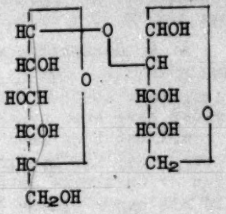


(III)

Oxidizing the disaccharide with bromine water yielded glucosido-3-mannonic acid (IV), hydrolysis of which yielded glucose, on the one hand, and mannonic acid, on the other. The mannonic acid was identified via its acetate.



(IV)



(V)

Oxidizing the calcium salt of glucosido-3-mannonic acid with hydrogen peroxide in the presence of an iron salt yielded glucosido-2-d-arabinose (V). Glucosido-2-d-arabinose yields only a hydrazone, which is evidence of the location of the connecting oxygen bridge in this disaccharide (1,2) and in the synthesized glucosido-3 mannose (1,3).

Thus we see that the position of the connecting oxygen bridge in glucosido--3-glucose remains unchanged during isomerization.

EXPERIMENTAL

1. Acetylating glucosido-3-glucose. A mixture of 20 g of glucosido-3-glucose (m.p. 162°), 10 g of dehydrated sodium acetate, and 150 g of freshly distilled acetic anhydride was refluxed, with frequent stirring, in a round-bottomed flask on a water bath for 3 hours. The hot liquid mass was added a drop at a time to 2 liters of ice water. The precipitated crystals were pulverized and kept under water until the next day to decompose the acetic acid. The filtered crystals were washed with cold water and recrystallized from ethyl alcohol. The yield was 31.4 g, or 78% of the theoretical.

M.p. 149-150°.

0.1319 g subs.: 15.5 ml 0.1 N NaOH; 0.2798 g subs.: 32.9 ml 0.1 N NaOH. Found %: $COCH_3$ 49.40, 49.53. $C_{28}H_{38}O_{19}$. Calc. %: $COCH_3$ 49.25.

2. Isomerizing glucosido-3-glucose acetate. 30 g of the octaacetate of glucosido-3-glucose was placed in 400 ml of anhydrous chloroform in a 1-liter round-bottomed flask fitted with a reflux condenser, and 100 g of dry askanite was added. The resulting mixture was agitated in the cold for 10 days. Toward the end the contents of the flask were heated to 70°. The askanite was filtered out of the faintly colored solution, which was evaporated to a thick syrup. The residual mass crystallized after a few hours. Microscopic examination of the crystals after they had been recrystallized from ethyl alcohol showed that they were not homogeneous, being apparently contaminated with the original product. The crystals were finally purified chromatographically on alumina.

M.p. 142-143°; α_D^{20} + 35.6° (in chloroform).

0.1522 g subs.: 17.6 ml 0.1 N. NaOH; 0.1997 g subs.: 23.2 ml 0.1 N NaOH. Found %: $COCH_3$ 50.15, 49.99. $C_{28}H_{38}O_{19}$. Calc. %: $COCH_3$ 49.25.

The free disaccharide was secured by saponifying the disaccharide acetate.

M.p. 165°; $\alpha\ ^{20}_{D}$ + 27.9° (in water).

0.01 g subs.: 0.1 g camphor: Δt 11.3°; 0.01 g subs.: 0.1 g camphor: Δt 11.4°. Found: M 355, 350. $C_{12}H_{22}O_{11}$. Calc.: M 342.

3. Oxidation of the disaccharide and hydrolysis of the resulting acid. 18.5 g of the new disaccharide we had synthesized was dissolved in 300 ml of bromine water, the resulting solution being exposed to light for 5 days with frequent stirring. Then the boiling solution was neutralized with calcium carbonate. The excess calcium carbonate was filtered out, and the solution was evaporated to a minimum. Gradually adding absolute ethyl alcohol to the resulting solution threw down flocs of a calcium salt of the bionic acid. The precipitate was filtered out and recrystallized from hot water to refine it. The yield was 16.3 g, or 81% of the theoretical.

0.2989 g subs.: 0.0210 g CaO; 0.3595 g subs.: 0.0294 g CaO. Found %: Ca 5.01, 5.87. $(C_{12}H_{21}O_{11})_2Ca$. Calc. %: Ca 5.30.

Precipitating the calcium from 5 g of the calcium salt with a calculated quantity of oxalic acid, followed by evaporating the filtered solution, yielded the bionic acid as a syrup. Then the bionic acid was boiled with a 5% solution of sulfuric acid to decompose it. The solution was neutralized, while boiling, with calcium carbonate and then filtered. Gradually adding absolute ethyl alcohol to the thickened solution threw down flocs of calcium mannonate. The calcium salt was purified by recrystallization from hot water.

After the calcium mannonate was filtered out, the solution was boiled with 5 ml of acetic acid and 5 g of pheylhydrazine. Yellow crystals settled out of the solution as it cooled. The crystals were filtered out and purified by recrystallization from ethyl alcohol. The melting point of the pure substance was 204 - 206°. The mixed melting point with a known sample of the glucosazone exhibited no depression.

4. Oxidizing glucosido-3-mannonic acid. 5 g of the calcium salt of glucosido-3-mannonic acid was dissolved in 100 ml of water. Solutions of 1.5 g of ferric sulfate in 20 ml of water and 1.9 g of barium acetate in 20 ml of water were added to the resulting solution after it had been heated to 70°. The reaction mixture was vigorously stirred, and 30 ml of a 30% perhydrol solution was gradually added. Three hours later another 10 ml of perhydrol was added to the solution. Then the precipitate was filtered out, and the solution was evaporated at reduced pressure to the thickness of a syrup. The syrup was mixed with 300 ml of a 1:1 methanol-acetone mixture. The insoluble matter was filtered out of the solution, which was evaporated to syrupy thickness. Yellow crystals were thrown down when the residue was mixed with absolute methanol. The next day the crystals were filtered out and dried. The yield was 1.7 g, or 50% of the theoretical.

M.p. 149-150°; $[\alpha]^{20}_{D}$ + 29.5° (in water).

0.0895 g subs.: 0.1416 g CO_2; 0.0484 g H_2O; 0.1009 g subs.: 0.1542 g CO_2; 0.0621 g H_2O. Found %: C 42.93, 42.20; H 6.01, 6.90. $C_{11}H_{20}O_{10}$. Calc. %: C 42.30; H 6.41.

Acetylating glucosido-2-d-arabinose.

M.p. 138-140°; $[\alpha]_D^{20}$ + 46.6° (in chloroform).

0.1045 g subs.: 12.4 ml 0.1 N. NaOH; 0.1510 g subs.: 17.6 ml 0.1 N solution of NaOH. Found %: $COCH_3$ 49.85, 50.21. $C_{25}H_{34}O_{17}$. Calc. %: $COCH_3$ 49.60.

When glucosido-2-d-arabinose was boiled with phenylhydrazine in the presence of acetic acid, followed by evaporation of the solution to small volume, the crystals of glucosido-2-d-arabinose hydrazone settled out; they were refined by recrystallization from alcohol. M.p. 177-181°.

0.1259 g subs.: 7.9 ml N_2 (15°, 738 mm); 0.1518 g subs.: 9.8 ml N_2 (15°, 738 mm). Found %: N: 7.25, 7.49. $C_{17}H_{26}O_9N_2$. Calc. % N 6.96.

The glucosido-3-mannonic acid was boiled with dilute sulfuric acid, glucose and mannonic acid were produced. The resulting solution was neutralized with calcium carbonate and filtered. A few milliliters of absolute ethyl alcohol were added to the thickened filtrate, causing flocs of calcium mannonate to settle out.

0.1579 g subs.: 0.0211 g CaO; 0.2489 g subs.: 0.0315 g CaO. Found %: Ca 9.57, 9.05. $(C_6H_{11}O_7)_2Ca$. Calc. %: Ca 9.30.

Decomposing the calcium mannonate with a calculated quantity of oxalic acid, followed by evaporating the filtered solution, yielded crystals of the lactone of mannonic acid, with a m.p. of 149-150°; $[\alpha]_D^{20}$ + 50.8° (in water), which agrees with the figures in the literature [4]. The mixed melting point with a known sample of the lactone of mannonic acid exhibits no depression.

0.1500 g subs.: 0.2525 g CO_2. 0.0747 g H_2O; 0.2110 g subs.: 0.3597 g CO_2; 0.0939 g H_2O. Found %: C 46.09, 46.61; H 5.51, 5.01. $C_6H_{10}O_6$. Calc. %: C 46.05; H 5.68.

Phenylhydrazide: m.p. 213-214°; $[\alpha]_D^{20}$ + 15.8° (in water).

0.2201 g subs.: 20.3 ml N_2 (16°, 740 mm); 0.3510 g subs.: 32.4 ml N_2 (16°, 740 mm). Found %: N 9.98, 10.09 $C_{12}H_{18}O_5N_2$. Calc. %: N 9.75.

The tetraacetate of mannonolactone had a m.p. of 119-120°; $[\alpha]_D^{20}$ + 51.4° (in chloroform). The mixed melting point with a known sample of the tetraacetate of mannonolactone exhibited no depression.

0.1020 g subs.: 11.5 ml 0.1 N NaOH: 0.1100 g subs.: 12.6 ml 0.1 N. NaOH. Found %: $COCH_3$ 49.01, 49.33. $C_{14}H_{18}O_{10}$. Calc. %: $COCH_3$ 49.65.

SUMMARY

1. Glucosido-3-mannose has been produced by agitating a chloroform solution of acetylated glucosido-3-glucose with askanite.

Glucose-3-mannose has been synthesized from acetylated glucosido-3-mannose.

2. Oxidation of the calcium salt of glucosido-3-mannonic acid with hydrogen peroxide yields glucosido-2-d-arabinose.

3. The glucosido-3-mannose and glucosido-2-d-arabinose have been identified via several of their derivatives.

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SYNTHESIS AND PROPERTIES OF 1,1-DIPHENYLPROPENE-1 OXIDE

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It is common knowledge that one of the principal methods of preparing alpha oxides is the reaction of alkalies with the halohydrins of alpha glycols. The conditions required for carrying out this reaction and the latter's velocity vary with the nature and concentration of the bases employed, and particularly with the structure of the original halohydrins. The aliphatic alpha oxides are produced by processing the respective halohydrins with aqueous, and even better, with alcoholic solutions of alkalies, comparatively little heat being required [1]. It is even easier to produce alpha oxides with aromatic radicals, some of them being produced when ether solutions of the respective halohydrins are merely agitated with powdered potassium hydroxide [2].

Eltekov [3] showed that the aliphatic alpha oxides which have a tertiary carbon atom in the oxide ring are hydrated very energetically, a large quantity of heat being evolved in some instances (isobutylene and tetramethylethylene oxides). N. A. Prilezhaev [4] secured the oxide of 2-methylhepten-2-one-6, which added water so quickly as to hinder its isolation. When the oxide ring contains primary or secondary carbon atoms, the oxides are hydrated very much more slowly, some of them requiring prolonged heating to 100° under pressure. The weight of the oxide molecules likewise affects their reaction with water [3]. Provided the structures of the oxides are identical, the alpha oxides of higher molecular weight will be hydrated more quickly. It has also been found [5] that the reaction of alpha oxides with water is strongly catalyzed by the hydrogen ions of acids, thus hydrating many oxides at ordinary temperature.

Another interesting feature of alpha oxides that is of practical importance is their ability to undergo isomeric transformations into aldehydes or ketones, depending upon the location of the oxide ring [6]. This latter process requires differing conditions that vary with the structure of the alpha oxides, and, conversely, under different conditions the alpha oxides may be isomerized into aldehydes or ketones or mixtures of the two [7]. The alpha oxides are isomerized exceptionally readily when certain substances are present, which catalyze this reaction, particularly acids [8]. The phenyl radical greatly increases the tendency of the oxides to undergo hydration and isomeric transformations. Phenylethene, 3-phenylpropene-1, 2-phenylpropene-1, and other alpha oxides, for example, are isomerized to the respective aldehydes or ketones by the action of hydrogen ions, as well as when they are distilled at atmospheric pressure, while 1,1-di-phenylethene is converted into the isomeric diphenylacetaldehyde even when distilled in vacuo [9].

The reports on 1,1-diphenylpropene-1 oxide are contradictory, however. Stoermer [10] heated 1,1-diphenyl-2-phenoxypropanol-1 $-(C_6H_5)_2COH-CH(OC_6H_5)CH_3$ with alcoholic potassium hydroxide to 220° under pressure and secured a mixture of products, one of which was a crystalline substance with a m.p. of 67° and a b.p. of 300° (with slight decomposition). The author believed that this compound was 1,1-diphenylpropene-1 oxide, which is not convertible into the isomeric

ketone, but Stoermer's findings are obviously wrong. Levy and Lagrave [11] also secured 1,1-diphenylpropene-1 oxide by oxidizing that hydrocarbon with benzoyl peroxide. According to them, this oxide is a crystalline substance, melting at 34° and isomerizing to 1,1-diphenylpropanone-2 when distilled slowly at atmospheric pressure.

One of the present authors [12] brominated 1,1-diphenylpropanol-1 in 80% acetic acid and secured a high yield of 1,1-diphenyl-2-bromopropanol-1. This bromohydrin was unknown in the literature, and we were interested in learning how it behaved with an alkali and in continuing a study of the properties of the 1,1-diphenylpropene-1 oxide that we expected to prepare:

$$(C_6H_5)_2C(OH)CHBrCH_3 \rightarrow (C_6H_5)_2C\!\!<\!\!\!\!>\!\!CHCH_3 + HBr.$$
(O)

The action of an alcoholic solution of KOH upon the bromohydrin in ethyl alcohol yielded an oily product, which yielded two substances when distilled. The first one boiled at 131-132° (2 mm), its analysis being the equivalent of $C_{15}H_{14}O$. When we added this substance to a 0.1 N solution of sulfuric acid, we secured a crystalline compound with a m.p. of 90-90.5°. Its analysis was equivalent to $C_{15}H_{16}O_2$, which is doubtless the formula of 1,1-diphenylpropane-diol-1,2 in this instance. In our experiment the only way for that glycol to be formed is by hydration of the saponification product of the bromohydrin – 1,1--diphenylpropene-1 oxide:

$$(C_6H_5)_2C\!\!<\!\!\!\!>\!\!CHCH_3 \rightarrow (C_6H_5)_2COHCHOHCH_3.$$
(O)

It should be noted that this oxide is also hydrated slowly in pure water, but is not hydrated in an alkaline medium.

The second substance, which distilled at 146-146.5° (2 mm), soon crystallized, with a m.p. of 43-44°. It exhibited no active hydrogen and reacted with semicarbazide. The analysis of this substance was the equivalent of $C_{15}H_{14}O$, which could only be the formula of the ketone formed by the isomerization of 1,1-diphenylpropene-1 oxide:

$$(C_6H_5)_2C\!\!<\!\!\!\!>\!\!CHCH_3 \rightarrow (C_6H_5)_2CHCOCH_3.$$
(O)

The structure of the synthesized compound was finally established by oxidizing it with nitric acid and a 1% permanganate solution. The oxidation products were found to contain benzophenone and diphenylacetic, acetic, and formic acids, which is proof of the formula 1,1-diphenylpropanone-2.

It should be noted that the literature states [13] that 1,1-diphenylpropanone-2 exists in two modifications: a low-melting one (m.p. 44-46°) and a high-melting one (m.p. 61°). The former is sometimes produced in recrystallization from alcohol, changing into the second one upon long storage; the high-melting one is produced most often and is not converted into the first form. In our test all of the 1,1--diphenylpropanone-2 was secured with a m.p. of 43-44°, its melting point remaining the same after recrystallization from ethyl alcohol and after nine months of storage. Hence, heating the oxide to 135° (2 mm) isomerized it to the corresponding ketone –

1,1-diphenylpropanone-2, while it is hydrated in an aqueous medium, especially when hydrogen ions are present, yielding the glycol 1,1-diphenylpropanediol-1,2. Inasmuch as the yield of 1,1-diphenylpropene-1 oxide and of 1,1-diphenylpropanone-2 (or, if desired, of 1,1-diphenylpropanediol-1,2) is nearly quantitative, the method we have outlined may be used to advantage in producing these substances for organic synthesis.

EXPERIMENTAL

Action of an alcoholic alkali on 1,1-diphenyl-2-bromopropanol-1. The bromohydrin $(C_6H_5)_2C(OH)CHBrCH_3$ was secured by brominating the tertiary alcohol 1,1-diphenylpropanol-1 in 80% acetic acid; its m.p. was 57°.

59.5 g of the bromohydrin was dissolved in ethyl alcohol, and about 60 g of 20% alcoholic KOH was slowly added. The alcoholic solution was diluted with water, the oil that settled out being separated, and the residue extracted with ether. The oil was combined with the ether extract, and the ether was driven off after desiccation over calcined potash. The remaining faintly yellowish oily liquid, totalling 42 g, was distilled twice at 2 mm, the following fractions being collected: 1) 130-131°, 1.0 g; 2) 131-132°, 9.0 g; 3) 132-136°, 1.5 g; 4) 146-146.5°, 28.5 g; plus a residue of 2.0 g in the distilling flask.

Fraction 2, b.p. 131-132° (2 mm), was a colorless liquid with a faint odor, which was oxidized very slowly by a 1% permanganate solution, reacted with bromine (evolving HBr), did not evolve methane when reacted with methylmagnesium iodide, and did not react with semicarbazide.

n_D^{20} 1.5740; d_4^{20} 1.0739; MR_D 66.01. $C_{15}H_{14}O$. Calc. 63.71.

0.1894 g subs.: 0.5965 g CO_2; 0.1172 g H_2O; 0.1756 g, 0.3672 g subs.: 23.83 g benzene: Δt 0.20, 0.41°. Found %: C 85.89; H 6.92. M 189.37, 193.17. $C_{15}H_{14}O$. Calc. %: C 85.71; H 6.66. M 210.

Hydration of 1,1-diphenylpropene-1 oxide. 3 g of the oxide was added to 15 ml of 0.1 N sulfuric acid. Hydration commenced after 30 to 40 minutes of agitation, the entire flask being full of snow white crystals aggregated into stars after 24 hours had elapsed.

The crystals were readily soluble in ether, methanol, ethyl alcohol, benzene, and acetic acid, dissolving more sparingly in petroleum ether, from which they were recrystallized. Their m.p. was 90-90.5° after they had been dried in a desiccator over sulfuric acid.

0.0798 g, 0.0883 g subs.: 15.71 ml, 17.64 ml CH_4 (0°, 760 mm); 0.1116 g, 0.2963 g subs.: 20.99 g benzene: Δt 0.129, 0.311°. Found %: OH 15.04, 15.27. M 211.9, 233.3. $C_{15}H_{16}O_2$. Calc. %: OH 14.91. M 228.

Fraction 4, b.p. 146-146.5° (2 mm), crystallized within 3 hours, its m.p. being 43-44°; the melting point did not change after recrystallization from ethyl alcohol. It was freely soluble in methanol, benzene, and chloroform. It decolorized a 1% solution of $KMnO_4$ slowly and decolorized bromine faster than did the oxide, though with the liberation of HBr, as in the case of the oxide. It did not liberate methane when reacted with methylmagnesium iodide, but reacted with semicarbazide to form a semicarbazone, the m.p. of which was 163-163.5° after recrystallization from methanol.

n_D^{20} 1.5793; d_4^{20} 1.0813; MR_D 64.56. $C_{15}H_{14}O$. Calc. 64.28.

0.1737 g, 0.2019 g subs.: 0.5560 g, 0.6325 g CO_2; 0.1078 g, 0.1225 g

H_2O; 0.1157 g, 0.3568 g subs.: 22.29 g benzene: Δt 0.135, 0.395°. Found %: C 85.52, 85.63; H 6.8 6.79. M 198.1, 208.7. $C_{15}H_{14}O$. Calc. %: C 85.71; H 6.66. M 210.

Oxidizing 1,1-diphenylpropanone-2 with nitric acid. 24 ml of nitric acid (sp. gr. 1.3) and 15 ml of water were added to 4 g of the substance. The mixture was boiled for 5 hours and then carefully neutralized with potash, the volatile neutral products of oxidation being driven off with steam. The ether extract yielded benzophenone, the semicarbazone of which had a m.p. of 163.5-165°. The mixed melting point with the known product exhibited no depression. The salts of the acids were decomposed with weak sulfuric acid, and the volatile acids were driven off. The solution of these acids was concentrated and processed with silver carbonate. Heating threw down an abundant black precipitate, evidence of the presence of formic acid. Crystallization of the silver salts yielded three fractions, analysis of which gave the following results:

Fraction I 0.045 g subs.: 0.0225 g Ag; Fraction II 0.0971 g subs.: 0.0607 g Ag; Fraction III 0.0498 g subs.: 0.0321 g Ag. Found %: Ag 50.0, 62.51, 64.45. CH_3COOAg. Calc. %: Ag 64.64.

The residue left after the volatile acids had been distilled was extracted with ether. Driving off the ether left behind a thick, dark-red, resinous mass, out of which crystals of a non-volatile acid, slightly soluble in benzene, settled out 24 hours later. The resinous portion was slowly eluted in the cold with small portions of benzene, the acid then being recrystallized from the latter. The acid had a m.p. of 145-146° with partial sublimation, which agrees with the figures [14] given for diphenylacetic acid. Thus, oxidation yielded benzophenone and formic, acetic, and diphenylacetic acids.

Oxidizing 1,1-diphenylpropanone-2 with a 1% solution of permanganate. 600 ml of a 1% solution of permanganate was added to 4 g of the substance portionwise as it was decolorized (which occurred with great difficulty). The presence of benzophenone among the neutral reaction products was demonstrated by the following findings: m.p. 47.5-48°; no depression of the mixed melting point with a known sample of benzophenone; and semicarbazone m.p. 164 165°.

The salts of the acids were decomposed with sulfuric acid, and the volatile acids were distilled. Processing the solution of the volatile acids with silver carbonate yielded a minute black precipitate plus two fractions of silver salts.

Fraction I 0.1113 g subs.: 0.0679 g Ag; Fraction II 0.1207 g subs.: 0.0779 g Ag. Found %: Ag 61.06, 64.54. CH_3COOAg. Calc. %: Ag 64.64.

The non-volatile acids were extracted with ether; driving off the ether yielded a minute quantity of a crystalline acid that sublimed and had a m.p. of 144-145.5° after recrystallization from benzene.

Thus, oxidation of 1,1-diphenylpropanone-2 with a 1% permanganate solution yielded benzophenone and formic, acetic, and phenylacetic acids. The process takes place chiefly at the bond between the carbonyl group and the first carbon atom.

SUMMARY

1. It has been found that 1,1-diphenylpropene-1 oxide is produced with great ease, in a nearly theoretical yield, by 1,1-diphenyl-2-bromopropanol-1 with an alcoholic alkali.

2. 1,1-Diphenylpropene-1 oxide is isomerized to 1,1-diphenylpropanone-2 when distilled in vacuum at 135° (2 mm), and is hydrated very rapidly to 1,1-diphenylpropanediol-1,2 in an acid medium.

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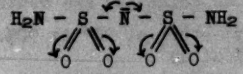
See Consultants Bureau English translation, p. 571.

THE HYDROLYSIS OF 2-METHYLIMIDOSULFONAMIDE AND MONOMETHYLSULFONAMIDE

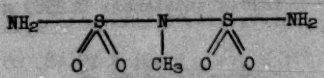
A. V. Kirsanov and Yu. M. Zolotov

The hydrolysis of 2-methylimidosulfonamide is much easier than that of the free imidosulfonamde [1]. Hydrolysis is nearly complete within 30 minutes in an approximately 0.25 N aqueous solution at 30°. When a weighed sample of 2-methylimidosulfonamide is dissolved in water at 15°, the solution being chilled to +5° within a minute and then evaporated in vacuum to dryness within 15 minutes at temperatures ranging from 0 to +5°, about 60% of the 2-methylimidosulfonamide is hydrolyzed. Hence, the experimental method of determining the velocity constant of hydrolysis, which was successfully employed for the free imidosulfonamide [1], is unsuited to a quantitative determination of the velocity constant of hydrolysis of 2-methylimidosulfonamide, though it is absolutely certain that 2-methylimidosulfonamide is hydrolyzed incomparably faster than the free imidosulfonamide is.

It has been previously established that the sodium salt of imidosulfonamide is hydrolyzed very slowly in boiling aqueous solutions [1]. We thus get the following series: sodium salt of imidosulfonamide (hydrolyzed rather slowly) – free imidosulfonamide (hydrolyzed rather quickly) – 2-methylimidosulfonamide (hydrolyzed extremely quickly). These findings are the basis for the conclusive deduction that the imidosulfonamide ion is stable in aqueous solutions, whereas the imidosulfonamide molecule is readily hydrolyzed in aqueous solutions. In the case of the sodium salt, the solution contains principally ions, and hydrolysis is slow. A solution of the free imidosulfonamide contains both ions and molecules, so that hydrolysis is faster. In the case of 2-methylimidosulfonamide, however, the solution contains nothing but molecules, so that hydrolysis is extremely rapid. It follows that the structure of the ion differs from that of the molecule. The stability of the imidosulfonamide ion is due to the fact that it possesses the following structure:



in contrast to 2-methylimidosulfonamide, the structure of which is:



In other words, the N – S distance (between the central nitrogen atom and the sulfur atom) is shortest in the sodium salt of imidosulfonamide, and greatest in 2-methylimidosulfonamide. It would be extremely interesting to check these conclusions by X-rays or electronographically.

Large numbers of the tetraalkyl sulfonamides, trialkyl sulfonamides, and asymmetrical dialkyl sulfonamides have been synthesized by now and thoroughly studied [2]. Not a single monoalkyl sulfonamide has been known, however. This is why the hydrolysis of 2-methylimidosulfonamide is highly interesting, since it ought to yield,

as we have shown in one of our previous papers, monomethylsulfonamide, as follows:

$$NH_2—SO_2—N(CH_3)—SO_2—NH_2 \xrightarrow{+H_2O} NH_2SO_2OH + NH_2SO_2NHCH_3.$$

As a matter of fact, we succeeded in securing a practically quantitative yield of monomethylsulfonamide from the hydrolysis products of 2-methylimidosulfonamide, its properties being described in the experimental section.

EXPERIMENTAL

Determination of the rate of hydrolysis of 2-methylimidosulfonamide. This was done as for the free imidosulfonamide [1]. I. A 0.4525 g sample was dissolved in 10 ml of water, heated for 30 minutes to 30 ± 0.05°, and so forth. Titration of the sulfamic acid required 2.29 ml of a 1N solution of sodium hydroxide. This indicated that 95.4% was hydrolyzed, i.e., nearly complete hydrolysis, in view of the fact that the accuracy of the method did not exceed 2-3%

II. A 0.4490 g sample was dissolved in 10 ml of water at 15°, the solution being chilled to +5° within a minute and then evaporated to dryness in vacuo at a temperature ranging from 0 to +5° for 15 minutes, and so forth. Titration required 1.43 ml of a 1N solution of sodium hydroxide. Thus 61.1% was hydrolyzed.

Synthesis of Monomethylimidosulfonamide

0.01 mol (1.89 g) of 2-methylimidosulfonamide was dissolved in 10 ml of water, and the solution was quickly brought to a boil, after which it was immediately cooled to room temperature and quickly evaporated in vacuo at 30° to dryness. The crystalline residue was extracted three times with 20 ml portions of absolute ethyl acetate. The residue left after the solvent had been driven off in vacuum consisted of 1.05 g of large colorless prisms with a m.p. of 63-65°. The yield was therefore 95% of the theoretical. After recrystallization from a large quantity (see below) of boiling benzene, thin snow-white, silky needles up to 30 mm long, m.p. 65.5-66.0° (uncorr.).

Monomethylimidosulfonamide is readily soluble in water, alcohol, acetone, and ethyl acetate. The aqueous solutions are neutral.

Its solubility in diethyl ether at 20° is 90%. Its solubility in boiling benzene is 0.265%, and 0.043% at 25°.

23.71 mg substance: 9.43 mg CO_2; 11.59 mg H_2O; 26.22 mg substance: 10.46 mg CO_2; 12.86 mg H_2O; 5.95 mg substance: 1.314 ml N_2 (21°, 755 mm); 6.10 mg substance: 1.350 ml N_2 (21°, 755 mm); 0.1216 g substance: 0.2589 g $BaSO_4$; 0.1322 g substance: 0.2809 g $BaSO_4$.

Found: % C 10.85, 10.87; H 5.47, 5.49; N 25.48, 25.53; S 29.23, 29.17. $CH_6O_2N_2S$.
Calc. %: C 10.90; H 5.49; N 25.45; S 29.12.

SUMMARY

1. It has been shown that 2-methylimidosulfonamide is hydrolyzed much faster than the free imidosulfonamide.

2. The hypothesis is advanced that the high rate of hydrolysis of 2-methylimidosulfonamide is due to the great distance between the central nitrogen atom and the adjacent sulfur atoms and that the stability of the sulfonamide ion in aqueous solutions is due to the lessening of this distance.

3. Monomethylimidosulfonamide has been synthesized and described.

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SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

XVIII. THE SULFONATION OF THIOPHENE

A. P. Terentyev and G. M. Kadatsky

In previous papers by one of the present authors [1] and in collaboration with L. A. Kasitsina [2] we have reported the results of our initial experiments on sulfonating thiophene and the alpha halogen thiophenes [3] with pyridine sulfotrioxide. They demonstrated that thiophene could be easily disulfonated under conditions in which its more acidophobic analogs - pyrrole and furan - yielded monosulfonic acids [1,2,4].

We have found that when thiophene is heated to 95-100° with pyridine sulfotrioxide, up to 28% of disulfo products are formed and up to 52% of the monosulfonic acid. Disulfonation is nearly complete (90% yield) at 130° (8 hours of catalysis). Using "acid" pyridine sulfotrioxide (adding 0.5% of sulfuric anhydride to the neutral reagent) speeds up this reaction and enables its temperature to be reduced to 95-100° (4-5 hours of catalysis).

The behavior of thiophene at high temperature very much resembles that of α-methylfuran, which also yields a disulfonic acid. The only way to effect monosulfonation of the latter compound was to react it for a long time with pyridine sulfotrioxide at 20-30° [2]. At this temperature the sulfonation of thiophene likewise involves the introduction of only one sulfo group:

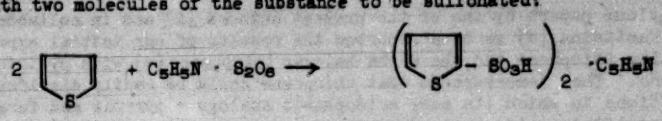
though we could not secure a higher yield than 50%.

Thus, the decisive factor affecting the course of the reaction is the temperature, so that some way of modifying the reaction, without raising the temperature, had to be found to secure a better yield of thiophenesulfonic acid. Employing the acid pyridine sulfotrioxide yielded nothing new. Only by resorting to a new sulfonating agent - pyridine bissulfotrioxide - did we secure the desired result.

Pyridine bissulfotrioxide was prepared by reacting together equimolecular quantities of pyridine sulfotrioxide and sulfuric anhydride. The latter was added either directly or dissolved in dichloroethane. The reaction was highly

exothermic. When the sulfotrioxide was used straight, the reagent was secured as a thick colorless liquid that solidified into a white crystalline mass with a m.p. of 83-85°. It fumed slightly when exposed to the air, reacted exothermally (but very quietly) with water, and underwent no change when heated to 150-160° for 24 hours. When the dichloroethane solution was used, a heavy liquid layer of the product separated out, which was converted into a low-fusible crystalline mass with difficulty. Each of these methods possesses its advantages. The first one yields the individual pyridine bissulfotrioxide, which dissolves in the substance to be sulfonated, the reaction taking place in a single phase. The second enables the sulfuric anhydride to be stored conveniently and its dosage to be measured accurately, but it involves retardation of the sulfonation reaction owing to the layering of the components.

Pyridine bissulfotrioxide reacted strongly with thiophene, yielding thiophenesulfonic acid. Sulfonation is 60% complete after 2 hours and 86% complete after 10. It is worthy of note that one molecule of this reagent reacts with two molecules of the substance to be sulfonated:



i.e., all the sulfuric anhydride is used in the reaction. When pyridine sulfotrioxide is used, 2 mols of it are required per mol of the substance, i.e. only half of the sulfuric anhydride goes to constitute the C – S bond, the rest remaining inactive, as it were.

The processing of the sulfo mass when the new reagent is employed is the same as that used with the pyridine sulfotrioxide. We have greatly simplified the procedure for preparing sulfochlorides. In the past, treating the reaction mass with barium carbonate yielded a barium salt, which was converted into a potassium salt, the latter being finally converted into the sulfochloride by the action of phosphorus pentachloride. We found that we could eliminate this sequence of reactions, treating the initial product with phosphorus pentachloride directly at 70-80° for 2 hours. The sulfochlorides are recovered from the reaction mass in the usual manner, the yields being satisfactory and the purity of the product adequate.

Thus, the use of pyridine sulfotrioxide and pyridine bissulfotrioxide to sulfonate thiophene has several advantages and produced better yields than the methods hitherto employed.

V. Meyer [5] and L. Weitz [6] used concentrated sulfuric acid, for example, diluting it more than 100 times with ligroin to prevent the complete tarring of the thiophene. The black sulfo mass had to be processed at once, as it too tarred completely when allowed to stand. The yield of the thiophene sulfonate was about 45%. Use of fuming sulfuric acid [7] yielded similar results.

V. Steinkopf and T. Hopner [8] used chilled chlorosulfonic acid and obtained a 65% yield of the sulfochloride. But their procedure was also unsatisfactory, since no more than 15% (of the theoretical quantity) of the sulfochloride was recovered when the reaction mass was decomposed with ice. The rest of the sulfochloride was secured by neutralizing the aqueous layer with soda and processing the desiccated mixture of sodium thiophenesulfonate, sodium sulfate, and sodium chloride with phosphorus pentachloride.

V. Meyer [9] and H. Jackel [10] secured salts of thiophenesulfonic-2,4 acid by sulfonating barium thiophenesulfonate with oleum, followed by processing of the sulfo mixture. V. Steinkopf and T. Hopner [8] sulfonated the sulfochloride rather than the salt with 7% oleum, securing a low yield of a mixture of 2,4- and 2,5-disulfo products.

Thus, the use of "acid" pyridine sulfotrioxide at high temperature effects a single-stage synthesis of thiophenylsulfo derivatives, replacing the previous two-stage syntheses. The yield obtained is high, producing a mixture of the 2,4 and 2,5 isomers, with the former predominating. At a low temperature all the sulfonating agents we have employed yield alpha sulfo products.

EXPERIMENTAL

Thiophenylsulfonic-2 Acid

Sulfonation with pyridine sulfotrioxide. Synthetic thiophene was used in sulfonation. B.p. 83.7-84° at 748 mm; d_4° 1.0607; n_D° 1.5238.

2.75 g of thiophene and 5.1 g of pyridine sulfotrioxide were sealed into an ampoule. After the latter had lain for a month at 20-30°, a white crystalline mass formed. The usual processing with barium carbonate and steam distillation of the pyridine was followed by evaporation of the filtrate, the barium salt being dried at 130°. The yield was 3.8 g (50%, based on the thiophene used).

Sulfonation with pyridine bissulfotrioxide. A solution of 1.6 g of sulfuric anhydride in 16 ml of dichloroethane was gradually added, with stirring, to 3.2 g of pyridine sulfotrioxide. The mixture grew warm. The application of gentle heating is required to complete the reaction, a colorless layer of pyridine bissulfotrioxide being formed beneath the dichloroethane. Then the mixture was stirred as 3.1 g of thiophene was added, causing the mixture to grow warm. Ten hours later the mixture was treated with water at room temperature, and the dichloroethane layer was removed. The aqueous layer was treated with an excess of barium carbonate and evaporated to eliminate the pyridine. Filtration and evaporation yielded 7.37 g of the barium salt (86% of the theoretical yield, based on the thiophene used). Mercuration of the dichloroethane layer resulted in the nearly complete recovery of the unreacted thiophene.

Barium thiophenesulfonate is a finely crystalline white powder that is freely soluble in water. Reacting the salt with bromine water throws down an abundant precipitate of $BaSO_4$.

5.520 mg substance: 2.797 mg $BaSO_4$; 4.690 mg substance: 2.380 mg $BaSO_4$. Found %: Ba 29.82, 29.87. $C_8H_6O_8S_4Ba$. Calc. %: Ba 29.62.

The S- (α- naphythyl) - thiuronate was prepared by mixing together saturated aqueous solutions of naphthylthiurone chloride and the barium sulfonate. The precipitate was recrystallized from water. M.p. 174.5-175°.

5.305 mg substance: 0.3822 ml N_2 (29°, 741 mm). Found %: N 7.65. $C_{11}H_{18}O_3N_2S_3$. Calc. % N 7.19.

2-Thiophene sulfochloride. 1) This was prepared from the potassium salt by heating it to 100° for 2 hours with an excess of phosphorus pentachloride and then pouring the reaction mass over ice. The crystals that formed were filtered out. M.p. 28-31°, but 31-32° after recrystallization from petroleum ether (b.p. 20-40°). Steinkopf gives the m.p. as 31.5-33° [8], while Weitz gives 28° [8]. 6.4 g of pyridine sulfotrioxide was placed in a 50-ml round bottomed flask, and 3.2 g of sulfuric anhdryide was added. The mixture heated up spontaneously to 90°, being converted into a thick, colorless liquid, which

solidified into a crystalline white mass. M.p. 83-85° 4.5 g of thiophene was added to the resultant pyridine bissulfotrioxide, , and the mixture was stirred and allowed to stand at room temperature. Ten hours later 17.5 g of phosphorus pentachloride was added to the light-colored thick liquid, and the reaction mixture was heated to 70-80° for 2 hours. It was poured out over ice after it had cooled, and the crystalline sulfochloride filtered out. At room temperature it turned into a paste, which crystallized after 2 days of standing, m.p. 28-30°. The m.p. of the sulfochloride was raised to 31-32° by recrystallization from petroleum ether (b.p. 20-40°). The mixed melting point when mixed with the sulfochloride prepared by Method 1 exhibited no depression.

Thiophenesulfonamide was prepared by heating the sulfochloride with ammonium carbonate and extracting with ether. M.p. 144.5-146°. The melting points given in the literature are: 146-147° and 141° [8,5]..

3.210 mg substance: 0.2400 ml N_2 (29°, 747 mm). Found %: N 8.31. $C_4H_5O_2NS_2$. Calc. %: N 8.58.

Thiophenesulfanilide had a m.p. of 99.5-100° (from an aqueous-alcoholic solution). V. Meyer gives the m.p. as 96° [5].

5.993 mg substance: 0.3185 ml N_2 (30°, 754 mm). Found %: N 5.95. $C_{10}H_8O_2NS_2$. Calc. %: N 5.88.

SUMMARY

It has been shown that reacting thiophene with pyridine sulfotrioxide at 20-30° produces thiophenesulfonic-2 acid (50% yield). At a temperature of 95-100° the monosulfonation is paralleled by the formation of a disulfo acid. The reagent is utilized nearly quantitatively at 130°, as well as when an "acid" reagent is employed, yielding a mixture of the 2,4 and 2,5 isomers of thiophenesulfonic acids.

It has been shown that pyridine yields a compound containing two SO_3 molecules: pyridine bissulfotrioxide, a powerful sulfonating agent that can be employed to sulfonate various acidophobic compounds. It sulfonates thiophene without any tarring at 20-30°, with an 86% yield of thiophenesulfonic-2 acid.

It has been shown that the primary products of sulfonation with pyridine sulfotrioxide and pyridine bissulfotrioxide may be used instead of the potassium salts to secure the acid chlorides of sulfonic acids. This method affords high yields.

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SYNTHESES OF POLYCYCLIC COMPOUNDS

XVI. SYNTHESIS OF THE MESO DERIVATIVES OF ANTHRACENE, USING ORGANOLITHIUM COMPOUNDS

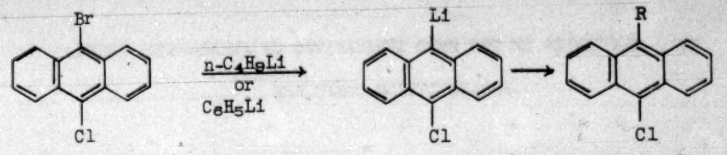
B. M. Mikhailov and V. P. Bronovitskaya

One of the present authors [1] has previously found that the reaction of the meso derivatives of anthracene with n-butyllithium yields organolithium compounds of anthracene, which may be used successfully for synthesis, as has been illustrated in several instances. The present paper reports the results of work on the development and improvement of the synthesis of anthracene derivatives by means of organolithium compounds, as well as the elucidation of various problems related to the exchange reactions of a halogen and lithium in the anthracene series.

Basing ourselves on the experimental production of organolithium compounds from 9-bromoanthracene and 9,10-dibromoanthracene, we first resorted to n-butyllithium to secure an organolithium compound of 9-chloro-10-bromoanthracene. The subsequent action of various reagents upon the resultant 9-chloroanthryl-10-lithium gave us meso derivatives of 9-chloranthracene, but the product yields did not exceed 35-50% in the best of cases, and were exceedingly small in some instances. No more than 4.5% of the theoretical yield of 9-ethyl-10-chloroanthracene was secured, for example, when we reacted ethyl iodide with the lithium compound prepared from 9-chloro-10 bromoanthracene. These unsatisfactory results are doubtless due, as B. M. Mikhailov and T. K. Kozminsky have shown in the 1,2-benzanthracene series [2], to the fact that the n-butyl bromide formed in the double decomposition reaction between 9-chloro-10-bromoanthracene and n-butyllithium reacts, in turn, with the organolithium compound, thus withdrawing the latter from the zone of subsequent transformations. It was therefore likely that using phenyllithium instead of n-butyllithium would prevent this secondary reaction, inasmuch as bromobenzene does not react with organolithium compounds of the anthracene series. As a matter of fact, we were able to secure much higher yields of 9-chloroanthracene derivatives by synthesizing 9-chloroanthryl-10-lithium with phenyllithium and then reacting it with various reagents, than we had ever secured in our experiments in which n-butyllithium was used.

When we reacted 9-chloroanthryl-10-lithium with carbon dioxide, for example, we secured a 73% yield of 9-chloroanthracene-10-carboxylic acid (I, R = COOH) instead of the 36% yield when n-butyllithium was used, and reacting the product with methyl iodide yielded 88% of 9-methyl-10-chloroanthracene (I, R = CH_3),

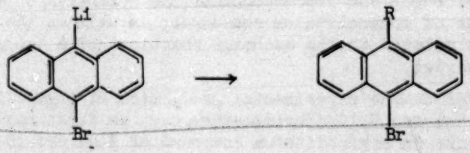
whereas only 50% was secured when n-butyllithium was used, while the yield of 9-ethyl-10-chloroanthracene (I, R = C_2H_5) was similarly raised from 4.5 to 47%.



(I)

R = COOH, CH_3, C_2H_5

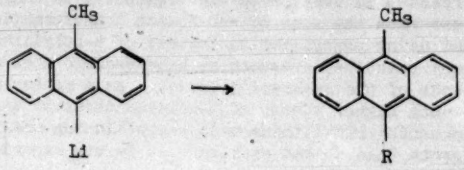
We found that the substitution of one atom of lithium for one atom of bromine took place no less smoothly when one equivalent of phenyllithium was reacted with 9,10-dibromoanthracene. Carboxylating the reaction products produced a 91% yield of 9-bromoanthracene-10-carboxylic acid (II, R = COOH), which was converted into 9-methyl-10-bromoanthracene (II, R = CH_3) by the action of methyl iodide, with a yield of 76%, and into 9-ethyl-10-bromoanthracene (II, R = C_2H_5) by the action of ethyl iodide.



(II)

R = COOH, CH_3, C_2H_5

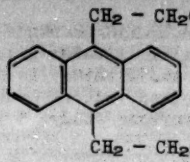
Reacting 9-methyl-10-bromoanthracene with phenyllithium yielded 9-methyl-anthryl-10-lithium, which was converted into 9-methylanthracene-10-carboxylic acid (III, R = COOH) by the action of carbonic acid, and into 9-methyl-10-ethylanthracene (III, R = C_2H_5) by the action of ethyl iodide. The action of methyl iodide upon the lithium compound of 9-methylanthracene, prepared with n-butyllithium, yielded 9,10-dimethylanthracene (III, R = CH_3).



(III)

R = CH_3, C_2H_5, COOH

We then investigated the ability of the two bromine atoms in 9,10-dibromo-anthracene to be replaced by lithium. Reacting 2 equivalents of n-butyllithium with 9,10-dibromoanthracene and then reacting the resulting organolithium compound with methyl iodide yielded about 40% of rather impure 9,10-dimethylanthracene, which was hard to purify, so that yield of the pure preparation did not exceed 16%; about 13% of the theoretical yield of 9,10-di- β -hydroxyethylanthracene (IV) was secured by reacting the reaction products with ethylene oxide.



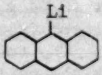
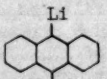
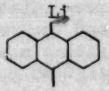
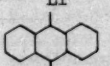
(IV)

The substitution of lithium for the second bromine atom in 9,10-dibromoanthracene requires fewer steps when 2 equivalents of phenyllithium are used. When the process was carried out for one hour at 50°, for example, and the reaction products then carboxylated, we secured 82% of the theoretical yield of 9-bromoanthracene-10-carboxylic acid, only 8% of the bromide being converted into the 9,10-dicarboxylic acid of anthracene; this proportion remained about the same when the reaction between the bromide and phenyl-lithium was carried out for 3 hours at 50°.

In contrast to the bromine derivatives, the chloride derivatives of anthracene do not enter into an exchange reaction of lithium for the halogen when they are reacted with phenyllithium. When 9-chloroanthracene was heated to 40° for 2 hours with 2 equivalents of phenyllithium, for instance, and the reaction mixture was then reacted with carbon dioxide, no anthracene-10-carboxylic acid was secured at all, while reacting 9-chloro-10-bromoanthracene with 2 equivalents of phenyl-lithium for 15 minutes, followed by carboxylation of the reaction products yielded nothing but 9-chloroanthracene-10-carboxylic acid.

The apparent instability of the organolithium compounds of anthracene secured when n-butyllithium is used, manifested in the decrease of the percentage of these compounds in the reaction mixture as the length of exposure to the reagents is increased (Table 1), was borne out by experiments on the reaction of bromine derivatives of anthracene with metallic lithium [1] in ether, in which organolithium compounds were either not produced at all or else produced with very poor yields, the principal reaction product being a hydrocarbon. Tests we ran in which the length of time the anthracene bromo derivatives were reacted with phenyllithium was varied indicated beyond any doubt, however, that the organolithium compounds of anthracene were stable in diethyl ether. We see in Table 1 that even two hours of heating at 40° has very little effect upon the percentage of organolithium compounds in the reaction mass.

TABLE 1*

RLi	Time, Minutes	Temperature	 %	 %	 %	 %
n-C_4H_9Li	5	15°	77	-	58	-
n-C_4H_9Li	15	40	58	36	80	-
n-C_4H_9Li	120	40	44	-	37	-
C_6H_5Li	15	15	-	73	91.3	13.8
C_6H_5Li	120	15	63.6	-	-	62.8
C_6H_5Li	120	40	71.7	69	88.3	62.8
C_6H_5Li	300	40	-	-	86	-

*See footnote on next page.

It is therefore obvious that the formation of hydrocarbons when bromine derivatives of anthracene are reacted with metallic lithium [1], such as the formation of anthracene from 9-bromoanthracene and lithium, is not due to the instability of the organolithium compounds in ether, but is caused by some unknown course of the reaction, which requires further study.

EXPERIMENTAL**

9-Chloroanthracene-10-carboxylic acid. 1 g of 9-chloroanthracene-10-bromoanthracene (m.p. 210.5-211°) [3] was added to a solution of phenyllithium, prepared in an ampoule from 0.9 g of bromobenzene, 0.09 g of lithium, and 5 ml of ether. The ampoule was carefully agitated at room temperature for 15 minutes, and then the brownish-yellow solution of the organometallic compound was poured over dry ice. Ether and water were added to the reaction products. The acid that settled out when the aqueous layer was acidulated was crystallized from alcohol. This yielded 0.64 g of the acid (73% of the theoretical) with a m.p. of 262-264°. After recrystallization from the same solvent, the substance consisted a yellow needles with a m.p. of 268.5-269.5°.

5.455 mg substance: 14.044 mg CO_2; 1.853 mg H_2O. Found %: C 70.38; H 3.80. $C_{15}H_9O_2Cl$. Calc. %: C. 70.18; H 5.53.

In an experiment in which n-butyllithium was used, 36% of the theoretical yield of an acid with a m.p. of 265-267° was secured after the reagents had interacted for 10 minutes and the reaction products had then been carboxylated.

9-Ethyl-10-chloroanthracene. An ether solution of 2.6 g of ethyl iodide was added to 10-chloroanthryl-9-lithium, prepared with phenyllithium as outlined above, and the reaction mixture was heated to 50° in a sealed ampoule for 3 hours. When heating was complete, the ether solution was washed with water, and the solvent was driven off. After being twice recrystallized from methanol, followed by crystallization from alcohol and then from acetone, the residue had a m.p. of 107-109° (0.39 g, or 47% of the theoretical). After another recrystallization from acetone the substance consisted of yellow leaflets with a m.p. of 109-110°. The m.p. of 9-ethyl-10-chloroanthracene is given in the literature as 111° [4]. When n-butyllithium was used, 4.5% of the theoretical yield of 9-ethyl-10-chloranthracene (m.p. 105-109°) was secured.

9-Methyl-10-chloroanthracene. An ether solution of 1.5 g of methyl iodide was added to 10-chloroanthryl-9-lithium, prepared similarly from the same quantities of reagents as specified above. Considerable heat was evolved, and a yellow precipitate was thrown down. The reaction mass was washed with water, the crystalline precipitate filtered out (0.54 g, m.p. 173-179°), the ether layer evaporated, and the residue crystallized from alcohol. This yielded 0.14 g of a substance with a m.p. of 173-179°. The total yield of 9-methyl-10-chloroanthracene was 0.68 g, or 88% of the theoretical. After recrystallization from a benzene - alcohol mixture, the 0.56 g of the substance had a m.p. of 179-180°. The 9-methyl-10-chloranthracene we had synthesized by reacting 9-methylanthracene with phosphorus pentachloride had a m.p. of 179-180° [3]. The yield of 9-methyl-10-chloranthracene (m.p. 174-177°) was 50% of the theoretical when n-butyllithium was used.

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*The percentage of organolithium compounds in the reaction mixture was estimated from the yields of carboxylic acids secured when the reaction products were reacted with carbon dioxide.

**All operations with organolithium compounds were performed in an atmosphere of nitrogen.

9-Bromoanthracene-10-carboxylic acid. 2 g of 9,10-dibromoanthracene was added to a phenyllithium solution prepared in an ampoule with 1.8 g of bromobenzene, 0.18 g of lithium, and 10 ml of ether. The mixture was agitated for 15 minutes at room temperature, and then the yellow-brown solution of the organometallic compound was poured over dry ice. Ether and water were added to the reaction products. Aciduating the aqueous layer yielded 1.65 g of an acid with a m.p. of 259-262° (91.3%). After the acid had been recrystallized from a benzene-alcohol mixture, it consisted of yellow needles with a m.p. of 265-267° (1.32 g) [1].

9-Methyl-10-bromoanthracene. 5 g of methyl iodide, diluted with ether, was added to 10-bromoanthryl-10-lithium, prepared as outlined above from 4 g of 9,10-dibromoanthracene and phenyllithium. Considerable heat was evolved, and a yellow precipitate was thrown down. The reaction mass was washed with water, and the crystalline precipitate was filtered out and crystallized from a benzene-alcohol mixture. This yielded 2.37 g of 9-methyl-10-bromoanthracene, m.p. 170-173°. The ether solution was evaporated, and the residue was recrystallized twice from a benzene-alcohol mixture. This yielded another 0.11 g of the bromide, m.p. 169-173°. The yield was 76% of the theoretical. The bromide had a melting point of 172-173° after the second recrystallization. A yield of 42.5% of the bromide was secured by reacting 9-methylanthracene with phosphorus pentachloride [3].

9-Ethyl-10-bromoanthracene. An ether solution of 2.6 g of ethyl iodide was added to 10-bromoanthracene-9-lithium, prepared with 2 g of 9,10-dibromoanthracene and phenyllithium. The ampoule was then sealed and heated to 50° for 3 hours. Then the reaction mass was washed with water, and the residue left after the solvent had been driven off was processed with several portions of a benzene-alcohol mixture. This yielded 0.63 g (37% of the theoretical) of a substance with a m.p. of 109-110° in the form of yellow needles. The literature gives the m.p. of 9-ethyl-10-bromoanthracene as 104° [5].

9,10-Dimethylanthracene. a) From 9,10-dibromoanthracene. 0.7 g of 9,10-dibromoanthracene was added to a n-butyllithium solution prepared with 0.6 g of n-butyl chloride, 0.08 g of lithium, and 10 ml of ether. Considerable heat was evolved and a dark-yellow precipitate of an organolithium compound was thrown down. The ampoule was carefully shaken for 15 minutes at room temperature, and then an ether solution of 1.8 g of methyl iodide was added. The reaction was accompanied by foaming and the precipitation of a light-yellow deposit. Half an hour later the reaction products were washed with water, the ether solution evaporated, and the residue crystallized from alcohol. This yielded 0.17 g of a substance with a m.p. of 162-175°. Recrystallization from a benzene-alcohol mixture yielded 0.07 g (16% of the theoretical) of a hydrocarbon with a m.p. of 183.5-184.5° as lustrous yellow needles that exhibited no depression of the melting point when mixed with a sample of 9,10-dimethylanthracene [6].

b) From 9-methyl-10-bromoanthracene. 0.5 g of 9-methyl-10-bromoanthracene (m.p. 172-173°) was added to a solution of n-butyllithium, prepared with 0.26 g of n-butyl chloride, 0.05 g of lithium, and 10 ml of ether. The reaction mixture was gently shaken at room temperature for 15 minutes, and then an ether solution of 0.8 g of methyl iodide was added. Some heat was evolved, and a crystalline yellow precipitate was thrown down. One hour later the reaction products were washed with water, the precipitate filtered out, and the ether solution evaporated. The residue was combined with the

crystalline precipitate and crystallized from a benzene-alcohol mixture. This yielded 0.25 g of a substance with a m.p. of 171-181.5°. Another recrystallization from a benzene-alcohol mixture yielded 0.2 g of a hydrocarbon (52.6% of the theoretical) with a m.p. of 183.5-184.5°.

9,10-Di-β-hydroxyethylanthracene. 0.7 g of 9,10-dibromoanthracene was added to a solution of n-butyllithium, prepared with 0.6 g of n-butyl chloride, 0.08 g of lithium, and 10 ml of ether. The ampoule was shaken for 15 minutes, and then gaseous ethylene oxide was passed through the reaction mass, the solution growing lighter and a voluminous yellow precipitate being thrown down. When the reaction was over, the alcoholate was decomposed with water, the precipitate (0.1 g with a m.p. of 210-215°) being filtered out, and the ether solution being evaporated to small volume. Another 0.03 g of a substance with a m.p. of 209-215° was recovered from the concentrated ether solution. Recrystallization of the combined precipitates from alcohol yielded 0.07 g (12.8% of the theoretical) of a substance as yellow needles with a m.p. of 220-223°. A second recrystallization from alcohol raised the substance's m.p. to 223.5-224.5°.

3.469 mg subs.: 10.350 mg CO_2; 2.224 mg H_2O. Found %: C 81.42; H 7.17. $C_{18}H_{18}O_2$. Calc. %: C 81.17; H 6.81.

9-Methylanthracene-10-carboxylic acid. 0.54 g of 9-methyl-10-bromoanthracene was added to a solution of n-butyllithium, prepared with 0.26 g of n-butyl chloride, 0.05 g of lithium, and 10 ml of ether. The reaction mixture was carefully shaken for 10 minutes at room temperature and then poured over dry ice. Ether and water were added to the reaction products, and the aqueous layer was separated and acidified. The precipitated acid (0.3 g, m.p. 203-206°) was crystallized from dilute alcohol. This yielded 0.2 g (42.5% of the theoretical) of the acid as lustrous yellow leaflets with a m.p. of 211-217°. Recrystallization of the acid from alcohol raised its m.p. to 219-220°.

3.406 mg subs.: 10.122 mg CO_2; 1.654 mg H_2O. Found %: C 81.10; H 5.43. $C_{15}H_{12}O_2$. Calc. %: C 81.33; H 5.12.

The same yield of 9-methyl-10-anthracenecarboxylic acid was secured by using phenyllithium, but in this experiment the mixture of 9-methyl-10-bromoanthracene was kept at room temperature for 1.5 hours.

9-Methyl-10-ethylanthracene. 1 g of 9-methyl-10-bromoanthracene was added to a solution of phenyllithium, prepared with 0.96 g of bromobenzene, 0.18 g of lithium, and 10 ml of ether. The ampoule was kept at room temperature, with stirring at intervals, for 2.5 hours, after which an ether solution of 1.75 g of ethyl iodide was added, and the ampoule was sealed and heated to 50° for 3 hours. The reaction products were washed with water, the ether solution evaporated, and the residue crystallized from alcohol. This yielded 0.54 g of a substance with a m.p. of 128-136°. Recrystallization from a benzene-methanol mixture yielded 0.46 g (57% of the theoretical) of a hydrocarbon with a m.p. of 139-141°. Still another recrystallization from the same solvents raised the m.p. of the substance to 142-144°. The literature gives the melting point of 9-methyl-10-ethylanthracene as 143-144° [7].

SUMMARY

1. A study has been made of the reactions of the meso halogen derivatives of anthracene with n-butyllithium and phenyllithium, which result in the formation of organolithium compounds of anthracene. It is advisable to use phenyl-

lithium in synthesizing these compounds, since its use eliminates the side reactions that take place when n-butyllithium is employed.

2. The organolithium compounds have been employed in the synthesis of various meso derivatives of anthracene.

3. The extent of the substitution of lithium for the two bromine atoms in the dibromo derivatives of anthracene is negligible when an excess of phenyllithium is used.

4. The meso chloro derivatives of anthracene do not react with phenyllithium.

5. The organolithium compounds of anthracene are fairly stable in an ether medium.

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*See C.B. English translation, p. 1395.
**See C.B. English translation, p. 359.

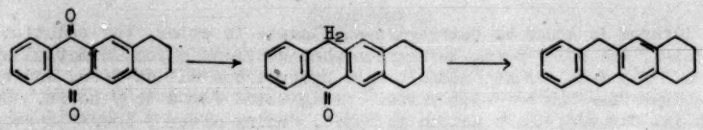
RESEARCHES ON THE NAPHTHACENES

I. ADDITION OF ALKALI METALS TO 1,2,3,4-TETRAHYDRONAPHTHACENE. TRANSFORMATIONS OF THE BIMETALLIC COMPOUNDS OF 1,2,3,4-TETRAHYDRONAPHTHACENE

B. M. Mikhailov and A. D. Chinaeva

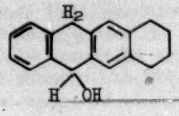
In synthesizing the derivatives of 1,2,3,4-tetrahydronaphthacene we used a method based upon the transformations of organometallic compounds produced by directly adding alkali metals to polycyclic compounds [1].

The initial hydrocarbon 1,2,3,4-tetrahydronaphthacene (III) was synthesized, with a 79% yield, from the readily available 1,2,3,4-tetrahydronaphthacenequinone (I) [2]. The quinone was first reduced by stannous chloride and hydrochloric acid to 1,2,3,4-tetrahydronaphthacenone 6 (II), which was then reduced with zinc dust and an alkali to the hydrocarbon.



(I) (II) (III)

A by-product in the synthesis of the hydrocarbon (III) was a minute quantity of 1,2,3,4,6,11-hexahydronaphthacenol-6 (IV), m.p. 174-175°.



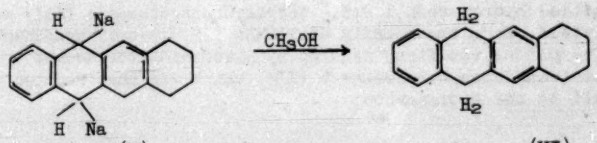
(IV)

The compound (IV) loses a molecule of water and is converted into 1,2,3,4-tetrahydronaphthacene (III) when it is heated to about 200° or boiled in a mixture of acetic anhydride and acetic acid, the yield of the hydrocarbon amounting to some 55% when the latter method is employed.

Braun, Bayer, and Fieser [3] previously secured a 10% yield of 1,2,3,4-tetra-

-hydronaphthacene (III) by reducing 1,2,3,4-tetrahydronaphthacenequinone catalytically, as well as by dehydrating the product (with an unsharp melting point of about 120°) secured by reducing the quinone (I) with zinc dust in the presence of ammonia and potassium hydroxide (though the yield was not given). The authors attribute the structure of 1,2,3,4,6,11-hexahydronaphthacenol-6 to the reduction product of the quinone (I), though our findings indicate that this substance's melting point is 174-175° rather than roughly 120°.

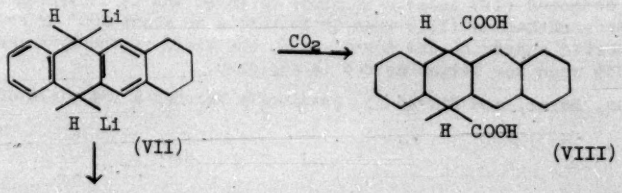
A study of the addition of alkali metals to 1,2,3,4-tetrahydronaphthacene has shown that sodium and lithium are added rather quickly to the hydrocarbon in ether, and even more rapidly in ethylene glycol dimethyl ether. The solution of the resulting organosodium compound of tetrahydronaphthacene is dark green whether the first or second ether is used as the medium. The action of methanol upon the organosodium compound (V) yielded 1,2,3,4,6,11-hexahydronaphthacene (VI)



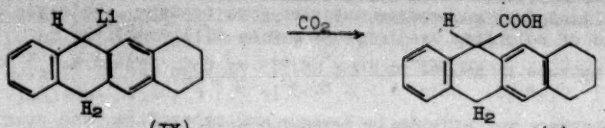
(V) (VI)

When lithium is added to tetrahydronaphthacene in ether, the solution is colored violet, its color being dark green when ethylene glycol dimethyl ether is employed. The metal is not added to the hydrocarbon all at once, addition occurring only after the reaction mixture is agitated for 6 to 9 hours. Once it has set in, however, the reaction is rapid, ending after 3 hours in ethylene glycol dimethyl ether. The action of carbon dioxide upon the dilithium compound of tetrahydronaphthacene (VII) produces a mixture of geometrical isomers of 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid (VIII), from which one of the isomers (cis or trans), with a m.p. of 198-204° (with decomposition), was isolated.

In the course of our research we found that the organolithium compound (VII) was unstable in ethylene glycol dimethyl ether, being partially hydrolyzed to 1,2,3,4,6,11-hexahydronaphthacyl-6-lithium (IX) when coming into contact with it. When the addition of the metal to the hydrocarbon was prolonged to 10 hours (from the onset of the reaction), the following carboxylation of the reaction products yielded 1,2,3,4,6,11-hexahydronaphthacene-6-carboxylic acid (X) in addition to the 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid.

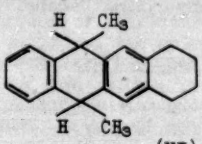


(VII) (VIII)



(IX) (X)

The action of methyl chloride upon the dilithum compound (VII) yields a mixture of the geometrical isomers of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene (XI), the cis and trans isomers of which were isolated in the pure state.



(XI)

Oxidation of the mixture of cis and trans isomers (XI) yielded 1,2,3,4-tetrahydronaphthacenequinone, which located the position of the methyl groups in the molecule.

EXPERIMENTAL

1,2,3,4-Tetrahydronaphthacene (III). A mixture consisting of 10 g of 1,2,3,4-tetrahydronaphthacenequinone (m.p. 216-217°) [2], 30 g of stannous chloride, 60 ml of concentrated hydrochloric acid, and 220 ml of glacial acetic acid was boiled for an hour, after which the brown-red reaction mixture was poured into cold water.

The light-yellow precipitate was filtered out and washed with water. The synthesized 1,2,3,4-tetrahydronaphthacenol had a m.p. of 140-142° without recrystallization. Then the wet precipitate was mixed with 20 g of zinc dust and 200 ml of 2N aqueous potassium hydroxide solution, and the mixture was boiled for 3 hours. The brown reaction mixture was quickly cooled, the resulting precipitate being filtered out and treated with 10% hydrochloric acid to remove the excess zinc dust. Then the substance was washed with water, dried, and crystallized from chloroform. This yielded 6.9 g of 1,2,3,4-tetra--hydronaphthacene as green-yellow leaflets with a m.p. of 243-244°. The yield was 77.9% of the theoretical. Fieser [3] gives the m.p. of 1,2,3,4-tetrahydro--naphthacene as 233°.

4.792 mg subs.: 16.323 mg CO_2; 3.053 mg H_2O. Found %: C 92.95; H 7.12. $C_{18}H_{16}$. Calc. %: C 93.06; H 6.94.

Adding methyl alcohol to the chloroform filtrate yielded 0.82 g of a substance with a m.p. of 173-175° and 0.34 g with a m.p. of 164-173°. Dehydration of these fractions with acetic anhydride and acetic acid (see below) yielded another 0.09 g of 1,2,3,4-tetrahydronaphthacene. The total yield of 1,2,3,4-tetrahydronaphthacene was 79%.

1,2,3,4,6,11-Hexahydronaphthacenol-6 (IV). The by-product with a m.p. of

173-175° that was isolated during the synthesis of 1,2,3,4-tetrahydronaphthacene was crystallized from chloroform and then from benzene. This yielded a substance in the shape of colorless needles with a m.p. of 174-175°.

6.065 mg subs.: 19.260 mg CO_2; 3.779 mg H_2O. Found %: C 86.66; H 6.97. $C_{18}H_{18}O$. Calc. %: C 86.36; H 7.24.

The substance was soluble in benzene and chloroform, and sparingly soluble in alcohol, acetone, and ether.

Dehydration of 1,2,3,4,6,11-hexahydronaphthacenol-6. A mixture of 1 g of 1,2,3,4,6,11-hexahydronaphthacenol-6, 23 ml of acetic anhydride, and 2 ml of glacial acetic acid was refluxed for 3 hours. When the reaction solution cooled, a crystalline substance with a m.p. of 238-240° was precipitated; it exhibited no depression with 1,2,3,4-tetrahydronaphthacene. The yield was 0.52 g, or 55.4% of the theoretical.

1,2,3,4,6,11-Hexahydronaphthacene (VI). A mixture of 0.2 g of 1,2,3,4--tetrahydronaphthacene, 0.056 g of sodium, and 5 ml of ethylene glycol dimethyl ether was placed in an ampoule, the air was driven off with nitrogen, and the ampoule was sealed and agitated for 12 hours. Then 2 ml of methanol diluted with 5 ml of ether was carefully added to the dark-green reaction mixture. The precipitate constituted the unreacted initial hydrocarbon. The colorless filtrate was diluted with water, the substance thrown down being filtered out (0.11 g) and recyrstallized twice from a benzene-alcohol mixture. M.p. 127-128°. The literature gives the m.p. of 1,2,3,4,6,11-hexahydronaphthacene as 128° [3].

1,2,3,4,6,11-Hexahydronaphthacene-6,11-dicarboxylic acid (VIII). 0.06 g of lithium, 0.5 g of 1,2,3,4-tetrahydronaphthacene, and 5 ml of ethylene glycol dimethyl ether were placed in a bottle filled with nitrogen. The reaction set in after 6 hours of agitation at room temperature, the mixture becoming dark-green and then turning to brown-red. The reaction mixture was agitated for 3 more hours after the color first appeared. Dry ice was added to the resulting organometallic compound, and then the carboxylation products were dissolved in water. The insoluble precipitate (40 mg) was filtered out, and the solution was acidulated with 10% hydrochloric acid. The resulting mixture of the cis and trans isomers of 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid was reprecipitated and dried in a vacuum desiccator. This yielded 0.42 g of acids with a m.p. of 162-176° (60.1% of the theoretical).

3.532 mg subs.: 9.650 mg CO_2; 1.964 mg H_2O. Found %: C 74.56; H 6.22. $C_{20}H_{18}O_4$. Calc.%: C 74.52; H 5.63.

Repeated recrystallization of the acid mixture from dilute alcohol isolated one of the cis-trans isomers of 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid as minute colorless needles with a m.p. of 198-204° (with decomposition).

3.522 mg subs.: 9.621 mg CO_2; 2.003 mg H_2O. Found %: C 74.54; H 6.36. $C_{20}H_{18}O_4$. Calc. %: C 74.52; H 5.63.

1,2,3,4,6,11-Hexahydronaphthacene-6-carboxylic acid (X). Ten hours of agitation after the onset of the reaction of the same quantities of substances, under the same conditions, as those described in the preceding experiment, yielded 0.49 g of a mixture of acids consisting of the cis-trans isomers of 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid and 1,2,3,4,6,11-hexahydronaphthacene-6-carboxylic acid, with a m.p. of 92-115°.

3.533 mg subs.: 10.296 mg CO_2; 2.141 mg H_2O. Found %: C 78.99; H 6.78. $C_{18}H_{18}O_2$. Calc. %: C 81.98; H 6.52; $C_{20}H_{18}O_4$. Calc. %: C 74.52; H 5.63.

Recrystallization of the mixture from alcohol and then from acetic acid yielded tetrahedral platelets of 1,2,3,4,6,11-hexahydronaphthacene-6-carboxylic acid with a m.p. of 187-196° (with decomposition).

3.841 mg subs.: 11.488 mg CO_2; 2.232 mg H_2O. Found %: C 81.62; H 6.53. $C_{19}H_{18}O_2$. Calc. %: C 81.98; H 6.52.

6,11-Dimethyl-1,2,3,4,6,11-hexahydronaphthacene (XI). 2 g of 1,2,3,4-tetrahydronaphthacene, 0.24 g of lithium, and 20 ml of ethylene glycol dimethyl ether were charged into a bottle filled with nitrogen. The reaction set in after the bottle had been agitated for 6 hours, agitation being continued for another 3 hours after that. Then the reaction bottle was connected to a two-tube adapter, one end of which was terminated by a calcium chloride tube, while the other was fitted with a glass tube extending to the bottom of the bottle, through which a current of anhydrous methyl chloride was passed. As the gas passed through the solution, the color of the organolithium compound disappeared, and lithium chloride was precipitated. When the reaction was over, the solvent was driven off, and the residue was extracted with benzene. The benzene solution was washed with water, the solvent driven off, and the 2.15 g of residue, a fluorescent yellow oil, was dissolved in alcohol. Within 24 hours 0.98 g of a crystalline substance with a m.p. of 87-135° was filtered out of the alcoholic solution. Another 0.34 g of a substance with a m.p. of 78-91° crystallized out of the filtrate after it had stood for some more time. The resultant fractions were dissolved in chloroform, 13 mg of the initial 1,2,3,4-tetrahydronaphthacene being recovered from the chilled solution. Adding acetone to the chloroform filtrate crystallized a colorless crystalline substance, the m.p. of which was 150.5-151° after recrystallization from alcohol, an acetone-alcohol mixture, and lastly ethyl acetate. Analysis indicated that this substance was the trans(cis) isomer of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene.

4.215 mg subs.: 14.121 mg CO_2; 1.708 mg H_2O. Found %: C 91.42; H 8.37. $C_{20}H_{22}$. Calc. %: C 91.54; H 8.45.

The hydrocarbon crystallized from acetone as colorless hexagonal platelets. It was freely soluble in benzene and chloroform, less so in acetone, alcohol, ethyl acetate, and methanol.

Repeated recrystallization of the crystalline fractions left after the isolation of the isomer of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene with a m.p. of 150.5-151°, first from acetone, then from an acetone-alcohol mixture, then from ethyl acetate, and finally from alcohol, yielded a substance as colorless needles with a m.p. of 125-126°, which proved to be another (cis or trans) isomer of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene upon analysis.

3.920 mg subs.: 9.776 mg CO_2; 2.332 mg H_2O. Found %: C 91.30; H 8.72. $C_{20}H_{22}$. Calc. %: C 91.54; H 8.45.

Oxidation of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene. 0.1 g of a mixture of the cis and trans isomers of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene, with a m.p. of 114-121°, was dissolved by heating it in 1 ml of glacial acetic acid, and 0.2563 g of chromic anhydride dissolved in acetic acid was added drop by drop to the boiling solution. The solution foamed violently. Then the reaction mixture was allowed to stand at room temperature for 15 hours. The precipitate was filtered out and washed with ether. The resulting substance had a m.p. of 216-217° and exhibited no depression of the melting point when mixed with a sample of the 1,2,3,4-tetrahydronaphthacenequinone synthesized earlier.

SUMMARY

1. Lithium and sodium are added to 1,2,3,4-tetrahydronaphthacene in ether or in ethylene glycol dimethyl ether.

2. The organolithium compound of 1,2,3,4-tetrahydronapthacene is hydrolyzed to a monolithium compound by ethylene glycol dimethyl ether.

3. The action of carbon dioxide or methyl chloride upon the dilithium compound of 1,2,3,4-tetrahydronaphthacene yields, respectively, 1,2,3,4,6,11-hexa--hydronaphthacene-6,11-dicarboxylic acid and the cis and trans isomers of 6,11--dimethyl-1,2,3,4,6,11-hexahydronaphthacene.

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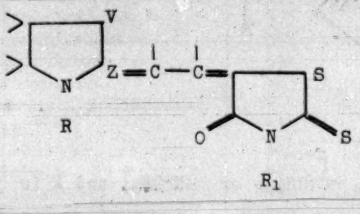
MEROCYANIN DYES THAT ARE DERIVATIVES OF RHODANINE

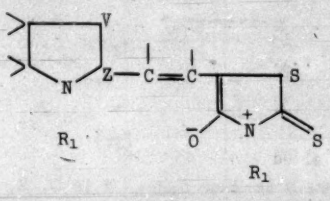
II. THE PROPERTIES OF DIMETHENYLMEROCYANINS WITH VARIOUS NITROGEN-CONTAINING HETEROCYCLIC RESIDUES

M. V. Deichmeister, Z. P. Sytnik, and E. B. Lifshits.

The dimethenylmerocyanins – derivatives of rhodanine (Ia and Ib) – are rather efficient optical sensitizers of silver halide photographic emulsions [1].



(Ia)

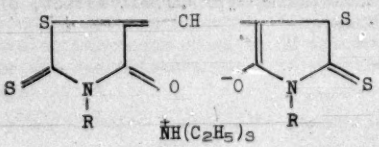


(Ib)

where R and R_1 are alkyls, aryls, or aralkyls; V is O, S, Se, $-CH=CH-$, $-C(CH_3)_2$, $=N-CH_3$, and so forth; and Z is carbon or the group $-CH=CH-C=$ (in the last instance there is no V group).

The patent literature [2] contains a large number of descriptions of such dyes and indicates the feasibility of using them as optical sensitizers for various regions of the spectrum. There is no information at all, however, on the variation of the photographic properties of these dyes with their structure, while the only reference to optical properties are a few comparisons made in Brooker's survey article [3]. The study of the optical and photographic properties of these merocyanins is of interest practically, as well as from the standpoint of the theoretical analysis of the color of inner ionoid compounds.

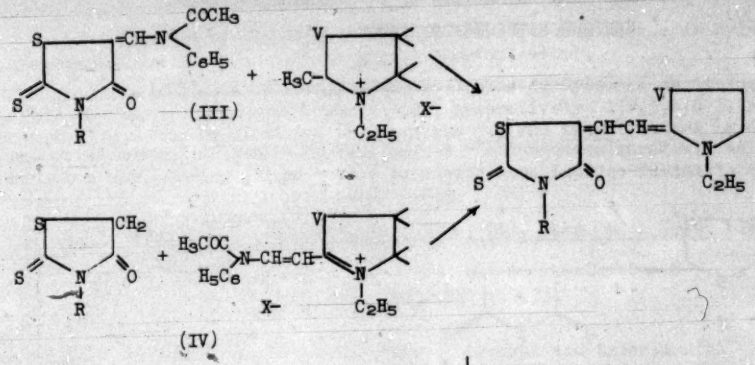
In the present paper we have explored the optical and photographic properties of the dimethenylmerocyanins – rhodanine derivatives – that differ in the nature of the nitrogen-containing heterocycle group. We have synthesized dyes of this type – derivatives of rhodanine and of its 3-ethyl derivatives – with the following groups containing an ethyl group attached to the nitrogen atom: 3,3-dimethylindolenine, thiazole, thiazdine, benzoxazole, β-naphthoxazole, benzothiazole, α-and β-naphtho-thiazoles, quinoline-(2 and 4), benzoselenazole, 5-methylthiodiazole-(1,3,4), pyridine-(2), and 1-methylbenzimidazole. We also synthesized monomethenyloxanines – derivatives of rhodanine and 3-ethylrhodanine (II).



(II)

where R is H or C_2H_5

Most of the foregoing merocyanins were synthesized by reacting the 5-(acetanilinomethylene)-rhodanines (III) with quaternary salts of the 2-methyl derivatives of the corresponding nitrogen-containing heterocyclic bases.



(III)

(IV)

where R is H or C_2H_5; V is O, S, Se, $-CH=CH-$, $-\overset{|}{C}(CH_3)_2$ or $=N-CH_3$; and X is an acid radical.

We were either unable to synthesize some dyes [the derivatives of pyridine-(2), the benzoxazoles, and the napththoxazoles] in this way, or else their yields were very low [the derivatives of 5-methylthiodiazole-(1,3,4), thiazoline, and quinoline-(2)]. These compounds were synthesized by condensing quaternary salts of the acetanilinovinyl derivatives of the heterocyclic bases (IV) with rhodanine or 3-ethylrhodanine [4]. The oxanine dyes (II) were synthesized by condensing the respective acetanilinomethylene derivatives with rhodanine or 3-ethylrhodanine in pyridine containing triethylamine [5].

If the structure of the merocyanins is intermediate between the Ia and Ib formulas, the absorption maximum is the arithmetical mean of the absorption maxima of the corresponding symmetrical carbocyanin and monomethenyloxanine (II) (cf [6-10,3]). As a rule, however, the real structure of the merocyanin molecule approaches the covalent form (Ia), which should lead to a hypsochromic shift of the absorption maximum from the values calculated above, as is the case in the asymmetrical carbocyanins. The magnitude of this hypsochromic effect will depend upon the closeness with which the structure of the dye approaches that of the formula (Ia), which in turn largely depends upon the basicity of the nitrogen-containing heterocyclic group [6].

Table 1 lists the absorption maxima of the two series of merocyanins we have synthesized: the derivatives of rhodanine and 3-ethylrhodanine, as well as of the corresponding carbocyanins and monomethenyloxanines. The dyes are listed in the order of diminishing hypsochromic effect, as given in the second column for each group of dyes.

TABLE 1

Nitrogen-containing heterocyclic group	λmax of the symcarbocyanin, (in mμ)	Merocyanins			
		Rhodanine derivatives		3-Ethylrhodanin derivatives	
		max, (mμ)	Hypsochromic effect, (mμ)	max, (mμ)	Hypsochromic effect, (mμ)
3,3-Dimethylindolenine	546	500	43	503	40
Benzoselenazole	570	522	33	524	31
α-Naphthothiazole	593	536	30.5	540	26.5
β-Naphthothiazole	595	540	27.5	542	25.5
Benzothiazole	557	520	28.5	524	24.5
β-Naphthoxazole	514	502	25	506	21
Benzoxazole	483	488	23.5	492	19.5
5-Methylthiodiazole-(1,3,4)	513	511	15.5	514	12.5
Thiazoline	445	480	12.5	482	10.5
Thiazole	543	530	11.5	532	9.5
Pyridine-(2)	560	540	10	542	8
Quinoline-(4)	705	612	10.5	614	8.5
Quinoline-(2)	604	564	8	565	7
1-Methylbenzimidazole	490	510	5	511	4

NOTE. The absorption maxima of the monomethenyloxanins (II) (R = H or C_2H_5) are located at 540 mμ in ethyl alcohol.

When we examine these results, the first thing we note is that the effect of the nature of a nitrogen-containing group upon the color of the merocyanins differs from that in the corresponding carbocyanins. N. N. Sveshnikov [10] has made similar observations in the merocyanins of 3-hydroxythionaphthene derivatives. As for the magnitude of the hypsochromic effect, it falls as the basicity of the nitrogen-containing heterocyclic group rises, as learned from a study of the absorption spectra of asymmetrical cyanins [11] and the ability of symmetrical carbocyanins to change into dibasic salts [12].

As we see from the table, the shift totals 40-43 mμ for merocyanins containing 3,3-dimethylindolenine radicals, and does not exceed 4-5 mμ for dyes with the most basic radical, benzimidazole. The merocyanins containing thiazoline, benzoxazole, and quinoline-(2) groups are somewhat out of line, their hypsochromic effect being smaller than one would expect from the degree of basicity of these groups. There is no fully satisfactory explanation for this fact at the present time. Thus, our findings confirm, on the whole, that the closer the structure of the tested merocyanins approaches to that of the covalent formula (Ia), the higher the color of these dyes. It should be noted that, in contrast to the corresponding dyes that contain 3-hydroxythionaphthene groups [13], the color of alcoholic solutions of salts of the monomethenyloxanines – derivatives of rhodanine and 3-ethylrhodanine – is practically unaffected by the addition of dilute mineral acids.

Most of the dimethylmerocyanins – rhodanine derivatives – are slightly

soluble in ethyl alcohol, which makes it hard to employ them as optical sensitizers. Attaching an ethyl group to the nitrogen atom of the rhodanine residue in these dyes increases their solubility in alcohol noticeably. The synthesized merocyanins act as sensitizers of silver halide emulsions. The most active are the dyes with thiazole, thiazoline and pyridine-(2) groups, the quinoline-(4) derivatives being much poorer sensitizers than all the other compounds, and also causing some fogging. The attaching of an ethyl group at the 3 position of the rhodanine residue always increases the dye's efficiency over dyes that are derivatives of unsubstituted rhodanine.

EXPERIMENTAL

Synthesis of Intermediates

3-Ethyl-5-(acetanilinomethylene)-rhodanine. A solution of 4.8 g of 3-ethylrhodanine and 6.45 g of diphenylformamidine in 35 ml of acetic anhydride containing 0.85 ml of triethylamine was refluxed for 1.5 hours. The next day the precipitated product was filtered out and washed with water and with alcohol. After it had been dried (weight 5.3 g, m.p. 128-129°), the product was crystallized from 60 ml of ethyl alcohol. The yield was 4.5 g (49% of the theoretical). Light yellow needles with a m.p. of 133° (with decomp.) [14].

Found %: N 9.00. $C_{14}H_{14}O_2N_2S_2$. Calc. %: N 9.14.

2-(β-Acetanilinovinyl)-pyridine ethiodide. A mixture of 0.35 g of 2-(β-anilinovinyl)-pyridine ethiodide [15], 0.074 g of ethyl orthoformate, and 2 ml of acetic anhydride was refluxed for 1 hour at 120°. The reaction solution was ice-chilled and treated with ether, the resultant precipitate being filtered out and washed with ether. The yield was 0.31 g (78.5%); m.p. 135-136° (with decomp.). The product was crystallized from butyl alcohol for analysis. This yielded 0.28 g of light-yellow platelets with a m.p. of 136-137° (with decomp.).

Found %: N 7.10. $C_{17}H_{19}ON_2I$. Calc. %: N 7.10.

Ethyl-p-toluenesulfonates of nitrogen-containing heterocyclic bases. These were synthesized by heating equimolecular quantities of the base and ethyl p-toluenesulfonate in a flask fitted with an air condenser and a calcium chloride tube under the following conditions: 4 hours at 140° for 2-methylbenzothiazole, 2-methylbenzoselenazole, 2,3,3-trimethylindolenine, 2-methyl-α-naphthothiazole, and 2-methyl-β-naphthothiazole; 5 hours at 140-145° for 2-methylthiazole; 1 hour at 120-130° for lepidine; and 1 hour at 110-115° for 1,2-dimethylbenzimidazole. The quaternary salts were used without further refining in synthesizing the dyes.

Synthesis of Merocyanins

The conditions governing the synthesis of the merocyanins, the melting points of the dyes, and the analysis results are given in Tables 2 and 3. The following notation is employed in these tables – for the initial products: I – rhodanine; II – 3-ethylrhodanine; III – 5-(acetanilinomethylene)-rhodanine [16]; and IV – 3-ethyl-5-(acetanilinomethylene)-rhodanine; for the ethyl-p-toluenesulfonates: V – of 2-methylbenzothiazole; VI – of 2-methyl-α-naphthothiazole; VII – of 2-methyl-β-naphthothiazole; VIII – of lepidine; IX – of 2-methylbenzoselenazole; X – of 2,3,3-trimethylindolenine; XI – of 2-methylthiazole; XII – 1,2-dimethylbenzimidazole; and XIII – 2-(β-acetanilinovinyl)-

-β-naphthoxazole; and for the ethiodides: XIV – 2-(β-acetanilinovinyl)-benzoxazole; XV – 2-(β-acetanilinovinyl)-5-methylthiodiazole-(1,3,4) [17]; XVI – 2-(β-acetanilinovinyl)-quinoline; XVII – 2-(β-acetanilinovinyl)-thiazole; and XVIII – 2-(β-acetanilinovinyl)-pyridine.

In every case the dye recovered upon chilling was filtered out, washed with water and with ethyl alcohol, and crystallized until its melting point was constant. The preparations were dried in vacuum at 50-60° to constant weight before being analyzed.

Triethylamine salt of 5-(4'-hydroxythiazolinethion-(2')-yl-5'-methylene)-thiazolidinethion-(2)-one-(4) [5]. A mixture of 0.55 g of 5-(acetanilinomethylene)-rhodanine, 0.53 g of rhodanine, 8 ml of pyridine, and 0.8 g of triethylamine was refluxed at 130° for 2 hours. After it had cooled, 200 ml of ether was added, and the precipitated dye was filtered out 6 hours later and washed with ether. Weight 0.38 g, m.p. 204-208° (with decomp.). 0.15 g (39.7% of the theoretical) was recovered after recrystallization from ethyl alcohol (1 g in 100 ml). Blue prisms with a m.p. of 226-228° (with decomp.). The salt was slightly soluble in benzene and ether, but readily soluble in ethyl alcohol and pyridine. The absorption maximum in ethyl alcohol was located at 540 mμ.

Found %: N 9.69. $C_{17}H_{27}O_2N_3S_4$. Computed %: N 9.68.

Triethylamine salt of 3-ethyl-5-(3'-ethyl-4'-hydroxythiazolinethion-(2')-yl-5'-methylene)-thiazolinethion-(2)-one-(4). Like the preceding dye, this was synthesized by heating a mixture of 0.3 g of 3-ethyl-5-(acetanilinomethylene)-rhodanine, 0.32 g of 3-ethylrhodanine, 4 ml of pyridine, and 0.4 g of triethylamine to 130° for 2 hours. Weight 0.35 g, m.p. 170-172° (with decomp.). Recrystallization from benzene (1 g in 150 ml) yielded 0.25 g (80.8% of the theoretical). Red-violet prisms with a m.p. of 177-179° (with decomp.). The salt was slightly soluble in ether, but readily soluble in benzene, ethyl alcohol, and pyridine. Its absorption maximum in ethyl alcohol was located at 540 mμ.

Found %: N 9.69. $C_{17}H_{27}O_2N_3S_4$. Calc. %: N 9.68.

The absorption maxima of all the synthesized dyes was measured with a Koenig-Martens spectrophotometer.

SUMMARY

1. 28 Dimethylmerocyanins – derivatives of rhodanine and 3-ethylrhodanine – have been synthesized, differing in the nature of their nitrogen-containing heterocyclic residues, plus two monomethenyloxanine dyes – derivatives of rhodanine and 3-ethylrhodanine.

2. It has been shown that the absorption maxima of the dimethylmerocyanins – rhodanine derivatives – are shifted to shorter wavelengths, compared to the arithmetical mean values calculated from the absorption maxima of the corresponding symmetrical carbocyanin and monomethenyloxanine. It has been found that the magnitude of this hypsochromic effect depends upon the basicity of the nitrogen-containing heterocyclic residue.

3. All the synthesized merocyanins are sensitizers of silver halide emulsions, the most effective being the dyes containing thiazole, thiazoline, and pyridine-(2) groups.

TABLE 2

Dye	g of III or IV	g of quaternary salt	Condensation conditions			
			Ml of C_5H_5N	Ml of absolute C_2H_5OH	Ml of C_4H_9OH	Ml of $(C_2H_5)_3N$
5-(3'-Ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]	III 0.5	V 0.59	10	–	–	–
3-Ethyl-5-(3'-ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]	IV 0.3	V 0.3	3	–	–	–
5-(3'-Ethyl-6',7'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]	III 0.28	VI 0.4	6	–	–	–
3-Ethyl-5-(3'-ethyl-6',7'-benzobenzothiazolinylidine-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]	IV 0.3	VI 0.4	3	–	–	–
5-(3'-Ethyl-4',5'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [4]	III 0.28	VII 0.4	–	10	–	0.14
3-Ethyl-5-(3'-ethyl-4',5'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [4]	IV 0.3	VII 0.4	3	–	–	–
5-(1'-Ethyldihydroquinolylidene-4'-ethylidene)-thiazolidinethion-(2)-one-(4) [2,4]	III 0.87	VIII 1.03	1.25	–	2.5	0.4
3-Ethyl-5-(1'-ethyldihydroquinolylidene-4'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]	IV 0.73	VIII 0.6	1.25	–	2.5	0.28
5-(1'-Ethyl-3',3'-dimethylindolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	III 0.28	X 0.26	–	–	5	0.14
3-Ethyl-5-(1'-ethyl-3',3'-dimethylindolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	IV 0.3	X 0.31	3	–	–	–
5-(3'-Ethylthiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	III 0.42	XI 0.45	–	–	6	0.21
3-Ethyl-5-(3'-ethylthiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	IV 0.6	XI 0.6	–	–	3	0.28
5-(1'-Methyl-3'-ethylbenzimidazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	III 0.55	XII 0.72	1	–	2	0.28
3-Ethyl-5-(1'-methyl-3'-ethylbenzimidazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	IV 0.3	XII 0.36	–	–	3	0.14
5-(3'-Ethylbenzoselenazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	III 0.28	IX 0.42	6	–	–	–
3-Ethyl-5-(3'-ethylbenzoselenazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	IV 0.3	IX 0.42	6	–	–	–

TABLE 2

Boiling time, min.	Yield, % of theory	Crystallization, solvent and quantity used, ml per g of dye	Appearance	Analysis: Melting point	Analysis: % N found	Analysis: Calculated: Empirical formula	Analysis: Calculated: % N
20	65.6	Pyridine 50	Red-violet needles	276°	-	$C_{14}H_{12}ON_2S_3$*	-
15	63.2	Glacial acetic acid 300	Dark-red needles	262-264	8.17	$C_{18}H_{16}ON_2S_3$	8.03
60	32.4	Alcohol + pyridine (4:1) 1100	Minute dark-brown needles	286-288	7.57	$C_{18}H_{14}ON_2S_3$	7.50
120	40.2	Glacial acetic acid 250	Minute violet needles	260-262	6.91	$C_{20}H_{18}ON_2S_3$	7.02
20	32.4	Glacial acetic acid 2000	Minute dark-green needles	288-290	7.57	$C_{18}H_{14}ON_2S_3$	7.75
180	55.3	Glacial acetic acid 330	Dark-red needles with a green sheen	274-276	7.21	$C_{20}H_{18}ON_2S_3$	7.02
60	28.6	Glacial acetic acid 40	Lustrous dark-blue leaflets	252-254	8.89	$C_{18}H_{14}ON_2S_2$	8.91
60	76.1	Benzene 120	Dark-blue needles	226-227	8.15	$C_{18}H_{18}ON_2S_2$	8.18
30	45.4	Ethyl alcohol 200	Bright-red needles	218	8.36	$C_{17}H_{18}ON_2S_2$	8.47
30	61.4	Ethyl alcohol 250	Pink leaflets	193-195	7.71	$C_{19}H_{20}ON_2S_2$	7.81
40	46.8	Ethyl alcohol 800	Brown prisms	239-241	10.35	$C_{10}H_{10}ON_2S_3$	10.35
40	58.7	Ethyl alcohol 100	Dark-blue prisms	216-217	9.30	$C_{12}H_{14}ON_2S_3$	9.38
60	18.9	Ethyl alcohol 680	Minute red-brown needles	217-218	13.00	$C_{15}H_{15}ON_3S_2$	13.23
120	52	Ethyl alcohol 400	Red needles	251-252	12.07	$C_{17}H_{18}ON_3S_2$	12.16
60	44.9	Glacial acetic acid 650	Violet prisms	240-241	7.69	$C_{14}H_{12}ON_2S_2Se$	7.62
30	46	Glacial acetic acid 400	Minute red-brown needles	258-260	7.00	$C_{16}H_{16}ON_2S_2Se$	7.08

*The per cent S was determined for this dye: Found 29.77, Calc. 30.0.

TABLE 3

Dye	g of acetanilinovinyl product	g of I or II	Condensation conditions: Ml of C_5H_5N	Ml of absolute C_2H_5OH	Ml of C_4H_9OH	Ml of $(C_2H_5)_3N$
5-(3'-Ethylbenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]	XIV 1.74	I 0.67	–	10	–	0.74
3-Ethyl-5-(3'-ethylbenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XIV 0.87	II 0.32	–	10	–	0.28
5-(3'-Ethyl-4',5'-benzobenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XIII 0.25	I 0.06	5	–	–	–
3-Ethyl-5-(3'-ethyl-4',5'-benzobenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XIII 0.53	II 0.16	5	–	–	–
5-(3'-Ethyl-5'-methylthiodiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XV 0.4	I 0.13	5	–	–	–
3-Ethyl-5-(3'-ethyl-5'-methylthiodiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XV 0.8	II 0.32	10	–	–	–
5-(1'Ethyldihydropyridylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XVIII 0.39	I 0.13	–	–	5	0.14
3-Ethyl-5-(1'-ethyldihydropyridylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XVIII 0.39	II 0.16	–	5	–	0.14
5-(1'-Ethyldihydroquinolylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [4]	XVI 1.32	I 0.47	10	–	–	–
3-Ethyl-5-(1'-ethyldihydroquinolylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]	XVI 0.44	II 0.19	5	–	–	–
3-Ethyl-5-(3'-ethylthiazolidinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	XVII 0.4	II 0.16	1.5	–	3	0.14
5-(3'-Ethylthiazolidinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [3]	XVII 0.4	I 0.13	1	–	2	0.14

TABLE 3

Boiling time, min.	Yield % of theory	Crystallization, solvent and quantity used, ml per g of dye	Appearance	Analysis			
				Melting point	% N found	Calculated	
						Empirical formula	% N
20	58.8	Glacial acetic acid 330	Bright-red leaflets	282°	9.11	$C_{14}H_{12}O_2N_2S_2$	9.20
15	52.7	Benzene 150	Dark-pink leaflets	228-230	8.48	$C_{16}H_{16}O_2N_2S_2$	8.42
120	56.6	Ethyl alcohol – pyridine (4:1) mixture 715	Red-violet needles	268-270	7.92	$C_{18}H_{14}O_2N_2S_2$	7.90
60	70	Glacial acetic acid 250	Minute red needles	302-304	7.50	$C_{20}H_{17}O_2N_3S_2$	7.32
30	31.6	Glacial acetic acid 220	Bright-pink needles	274-276	14.89	$C_{10}H_{11}ON_3S_3$	14.73
30	47.8	Ethyl alcohol 800	Red needles	244-246	13.48	$C_{12}H_{15}ON_3S_3$	13.40
30	56.6	Ethyl alcohol 600	Lustrous dark-blue prisms	218-220	10.39	$C_{12}H_{12}ON_2S_2$	10.59
30	75.3	Ethyl alcohol 50	Violet leaflets	162-164	–	$C_{14}H_{16}ON_2S_2$	–
360	46.7	Ethyl alcohol 12,500	Lustrous dark-blue leaflets	256-258	8.68	$C_{18}H_{14}ON_2S_2$	8.91
360	38	Benzene 100	Lustrous blue prisms	233-235	8.06	$C_{18}H_{16}ON_2S_2$	8.18
120	70	Ethyl alcohol 75	Brown leaflets with a blue sheen	163-164	9.38	$C_{12}H_{16}ON_2S_3$	9.32
60	71	Ethyl alcohol 400	Brown prisms	260-262	10.42	$C_{10}H_{12}ON_2S_3$	10.28

* The per cent S was determined for this dye: Found 21.77, Calc. 21.92.

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See C.B. English translation, p. 847.

SOME COMMENTS ON DETERMINING THE PURITY OF 2,5-DIMETHYLPYRROLE AND PYRROLE

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The Syntheses of Organic Preparations, Vol. 2, published in 1949, states: "Since 2,5-dimethylpyrrole forms no solid derivatives, the refractive index, n_D^{22} 1.500, may be employed as a criterion of the purity of the freshly distilled product."

This assertion is not entirely right. We have found that the freezing point may also be used as a criterion of the purity of 2,5-dimethylpyrrole. Investigation has shown that 2,5-dimethylpyrrole solidifies at +6.5° C. The apparatus for the freezing point determination consists of a test tube containing a glass stirrer and a thermometer (preferably graduated in tenths of a degree). Enough 2,5-dimethylpyrrole is poured into the test tube to immerse the mercury bulb of the thermometer in the liquid. The test tube thus equipped is placed within another test tube immersed in a beaker containing ice water. The thermometer readings are taken every 30 seconds. The temperature usually drops to +3.5-4.5°C, and then rises quickly to +6.5°, the contents of the test tube beginning to solidify at that instant. After some time has elapsed the temperature begins to drop, and the substance is so solid that stirring becomes impossible.

The 2,5-dimethylpyrrole was prepared by heating 2,5-dimethylpyrrole-monocarboxylate with soda lime [1].

Preliminary tests were also run to determine the freezing point of pyrrole, the tests being made in the apparatus described above, with the test tube immersed in a Dewar flask filled with dry ice. The freezing point of pyrrole is of the order of −27° C.

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MODERNIZATION OF MENDELEEV'S PERIODIC SYSTEM OF THE ELEMENTS

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1. Graphical representation of the periodic law - Mendeleev's periodic system of the elements, the brilliant consummation of a series of endeavors to systematize the elements that antedated Mendeleev - has, in turn, served as the starting point for numerous new attempts at systematization. We know of some 150 tables of the elements published after Mendeleev, 20 of which have been put forward by our own native chemists.

The motives behind these systematization endeavors differ. At times there is the desire to represent the periodic law more fully and more clearly, graphically speaking, plus an endeavor to define more accurately the position of various elements within the system or the analogies between them. Sometimes the changes introduced into the Mendeleev table are quite insignificant, while others involve a radical graphic reconstruction of the table. Many of the tables put forward are highly original and, by stressing individual regularities expressed by the periodic law, have a healthy core and hence, a raison d'etre. In most of these tables, however (especially in those published by foreign authors), the profound philosophical thought of the Mendeleev system and the latter's principal and distinct features: its grouping and its "stellate nature" (i.e., the surrounding of other elements that is specific for each element), in other words, everything that earned its merited triumph and gave it permanent significance is violated. The best table would be one that simply and clearly represented a maximum of the major physical and chemical properties of the elements, their electronic architecture, and their dialectical interrelationships. But even such an "optimum" table could not, in our opinion, encompass all the regularities embraced by the periodic law, the greatest law in the evolution of matter.

2. Nor is there any doubt that even in the classical Mendeleev table some features no longer satisfy the accumulated factual data or the objectives of a more thorough study of chemistry: both chemistry and the methods of chemistry have made considerable progress during the past 80 years.

As we see it, the following are among the weaknesses of the classical Mendeleev table.

a) The absence of electron stratification. The periodic system asserts periodicity, but does not provide a graphical representation of its basic cause - the recurrence of the electron structures.

b) The interrelationships (the nature of the analogies) between the elements of each group are not made clear. The elements of the major subgroup of Group V N,P,As, Sb, and Bi, for instance, are shown as analogs of equal value, which is not true; nor are the interrelationships between the elements of any subgroup and the elements in a subsidiary (auxiliary) subgroup of the same group revealed.

c) The degree of kinship between the major and subsidiary subgroups in any group is not indicated. For example, the degree of kinship between the manganese subgroup and the halogens is represented as the same as the degree of kinship between the scandium subgroup and the major subgroup of Group III (B, Al, Ga, In, Tl), which is far from being the case.

1) Hydrogen is placed either in Group I above the alkali metal (the older versions of the system) or in Group VII above the halogens (in the later editions), or is included in both Groups I and VII, or lastly, it is kept out of any group. Yet, all its properties, both in the atomic and ionic states, as well as its capacity as a simple substance, indicate that hydrogen belongs to Groups I and VII simultaneously. It is the distinguishing feature of Period 1 that the "transition" of properties from the typically metallic to the typically nonmetallic takes place in this period within the confines of a single amphoteric element, hydrogen, which is followed as a rule by an inert gas (helium) to complete the period. This also applies to helium, all of whose properties indicate that it ought to belong simultaneously to the beryllium subgroup and the subgroup of the inert gases.

e) The copper subgroup is assigned uniquely to Group I, which contradicts the maximum oxygen valency (+3) exhibited by the elements of this subgroup. Wheeler comments rather sharply on this: "Assigning the copper subgroup to Group I alienates a chemist and compels him to regard the periodic system of Mendeleev with an unfriendly eye [1]."

Wheeler may object that Mendeleev himself placed the copper subgroup in Group I at times and in Group VIII at others, thus emphasizing its dual nature and its right to belong to Groups VIII and I at the same time.

f) The Mendeleev table (like, moreoever, most of the other suggested tables) makes no provision for the lanthanides and the actinides; they are either placed in a special subtable, which interferes with an analysis of their interrelationships with other elements, or the lanthanides are placed in the same space as lanthanum, making an analysis of that sort impossible. Generally speaking, the exclusion of 25 elements from the table renders the entire system incomplete.

g) The elements of each group in the Mendeleev system are divided into 2 subgroups. Yet the system's groups should, of course, be "tripled" rather than "doubled" if the lanthanides and actinides are to be included in the table - and a rational system must include them - since the matallicity and the electronic structure of the lanthanides and actinides make them a "second subsidiary subgroup" of the elements of "f" family.

3) All the tables of the periodic system put forward during the past 82 years may be grouped into six major types [2]:

a) Checkerboard tables of the short form, i.e., based on an octet of groups. The original table of this type was Mendeleev's classical table of 1870.

b) Checkerboard tables of the long form, i.e., those consisting of 18 subgroups.

c) "Ladder" tables, stemming from Mendeleev's first table of 1869.

d) Spiral tables (two-dimensional), deriving from Hinrichs' system (1857).

e) Helical tables (three-dimensional), the first of which was Chancourtois' system of 1863.

f) Other systems.

4. A study and analysis of the 150 domestic and foreign tables of the elements referred to, many of which have been proposed by quite eminent scientists (Prof. Kurbatov, Prof. Nekrasov, Crookes, Werner, Bohr, Soddy, and others), cannot fail to convince one that none of them is a radical improvement upon the classical Mendeleev table, from the standpoint of satisfying modern requirements. In most of them the profound dialectical (and, hence, scientific) nature of the

Mendeleev system is violated, occasionally disappearing entirely. Notwithstanding the fact that the roots of periodicity are doubtless embedded in the structure of the atom, none of the systematizers has attempted to "link" the system of elements to the schema of electronic structure to "derive" the system from atomic structure.

The author of the present paper believes that Mendeleev's periodic system of the elements can and must be modernized without violating Mendeleev's basic design or its basic characteristics inherent in the system. This may be done upon the following assumptions.

1. The periodicity of the elements' properties depends largely upon the recurrence of the electronic structures. Hence, the periodic system can and must be "derived" from the atomic structure. The atom of any given element, which includes the electron configuration of the preceding element and in turn is a part of the electron configuration of the next higher elements, is necessarily dialectically interrelated and united with the system of elements as a whole. It is obvious that the unit can also be graphically combined with the whole (an electron with an atom of an element; an element's atom with the system), that is, a sort of "system-atom" can be established.

2. The dialectical spirallike nature of the development of matter and the transition of quantity into a new quality may also be represented graphically: the transition from one element to another takes place, on the whole, as a spiral (symbolizing the continuity of the development of matter), via the addition of a new electron to the shell and of a proton plus the number of neutrons required to make up the number (A - Z) to the nucleus. The gradual quantitative change in the number of electrons and their states (and, of course, the change in the number of nucleons in the nucleus) gradually results (at the periphery) in a new quality of the resultant new elements, and, after a full turn of the spiral, in an abrupt reproduction of the original element upon a new and higher level (i.e., in an element-analog).

3. All the specific features of the classical Mendeleev system, which has proved its worth as a scientific and philosophical generalization of chemical facts, must be retained. Hence, the "stellate nature" of the Mendeleev system and its octet of groups, i.e., the distribution of all the elements into 8 groups (with 2 subgroups of elements of the "s" family and 6 subgroups of the "p" family which is also best from the pedagogical standpoint, must be preserved. (The octet of groups is supported by Morozov's rule on the sum of the positive and negative valencies of the principal subgroups of Groups IV, V, VI, and VII, which totals 8, by the maximum observable positive element valency, 8, by the electron octet in various theories of the chemical bond, etc.)

The Mendeleev system of the elements, as modernized by us on the basis of the energy characteristics of atoms, consists of a radial-circular graph (see the chart on p. 227).

The various sections of the circumference (preferably done in color) represent the various energy levels or "states" of the electrons: s - p - d - f (the solid portions of the circumference representing levels that are being completed, while the dotted sections represent completed levels); the various series of similar levels - circumferences - constitute periods, separated by gaps. The element subgroups (series of electron analogs) are arranged along the radii. The system begins at the center, with the hydrogen atom, progressing spirally clockwise.

The radii of the "principal" element subgroups in the table are not arranged arbitrarily, their location stemming from the energy character of the subgroups.

As we know, the important constants of the atoms of the elements are: the first ionization potential (characterizing the reducing ability or "metallicity"), the electron affinity (characterizing the oxidizing ability or "nonmetallicity",) and the "electronegativity" (characterizing the overall tendency of the atom to eject or add an electron.)[1]

The mean ionization potential (in volts) of a subgroup or the equivalent mean ionization energy (in electron volts or kilocalories) and its mean electronegativity (in relative units) may be utilized in making a quantitative estimate of the energy nature of subgroups. A comparison of these figures is interesting. For the lithium subgroup (Group I), for example, they are 4.4 volts and 0.85, respectively.

For the carbon subgroup	(Group IV)	8 volts	and 1.92
" " fluorine "	(Group VII)	12.7 "	" 2.05
" " inert gases "	(Group VIII)	16.4 "	" 4

Rounding off these figures somewhat to:

4 volts and 1; 8 volts and 2.12 volts and 5; 16 volts and 4, we see that about the same jump of both the mean ionization potential (about 4 volts) and of the mean electronegativity (about 1) exists in the transition from the principal subgroup of Group 1 to the principal subgroups of Groups IV, VII, and VIII. This identical jump may be represented graphically by the same deflection angle (90°) of the radius representing the given subgroup. If we agree to place the lithium subgroup at the left-hand radius of the diameter, the carbon subgroup is located at right angles to it, the fluorine subgroup diametrically opposite to it, and the subgroup of the inert gases downward, at an angle of 270°, and this determines the basic structure of the table. The intermediate principal subgroups of Groups II, III, V, and VI may be arranged symetrically between the specified subgroups of Groups I, IV, and VII without introducing any appreciable error. Thus, the proposed modernization is based upon the quatitative energy characteristics of the atoms, Mendeleev having said that "every system founded upon numbers is to be preferred to others."

The Roman figures for the eight principal radii indicate the number of valence electrons (the number of solitary electrons in the atom in the latter's excited state), i.e., the maximum positive valence of the element. The Arabic figures (and their sign) indicate the maximum (+ or −) valence of the element, in terms of hydrogen.

The "intravalent" elements, i.e., those whose electron shells in process of completion (s and f electrons), constitute additional radii - subgroups. Falling into one or another of the eight groups, depending upon the maximum positive valency they exhibit, they constitute "overtones" of the principal "octave" as it were. It is pedagogically interesting to represent their greater or lesser kinship to the major subgroups in the system graphically; this may be done by using different angles of advance of the radii of the major and subsidiary subgroups, corresponding to the differences in the subgroup ionization potentials. (This difference is expressed in angular units). We see at once that only the two subgroups of Groups III and IV are fully akin, to the point where some scientists consider B-Al-Ga-In-Tl to be the "major" subgroup, for example, while

[1] Electronegativity is defined as the arithmetical sum of the ionization energy and the electron affinity, expressed in Cal per gram-atom. If we take the electronegativity of lithium as 1, we get the electronegativity of the other elements in relative units.

others regard B-Al-Sc-Y-La-Ac to be the major subgroup. The subgroups of the other groups, with the possible exception of IV, differ substantially (the halogens and the manganese subgroup, for instance). When we examine any group in the diagram, from the periphery to the center, we see that each subgroup at the left is more metallic than the one at the right, as in Mendeleev's classic table.

The various tiny circles denote both the electrons in various energy states and the elements of the families corresponding to these states.

The various kinds of lines used for the circumferences denote the course of the completion of the respective electron levels - "states". The complete circumference of the s level contains a maximum of 2 electrons or elements; the complete circumference of the p level six electrons or elements; the complete circumference of the d level ten; and the complete circumference of the f level 14.

The anomalies in the completion of the electron shells, the so-called electron "gaps" (the completion of the d level at the expense of the s level, and of the f level at the expense of the d level) are denoted by arrows. Spectroscopic data indicate that there are 9 such anomalies (these elements are: Cr, Cu, Nb, Pd, Ce, Tb, Pa, Am, and Bk).

In contrast to the paths chosen by most table constructors, who follow the line of least resistance in solving the problem of the arrangement of the lanthanides [i.e., by (a) not including them in the table at all, or (b) putting them in the same square as lanthanum, or (c) placing them in a separate little table outside the main table itself], the lanthanides are an organic part of this proposed modernization. Like the "actinides," they constitute "second subsidiary subgroup-radii," consisting of elements of the f family.

In view of the so-called "internal periodicity" within the lanthanide family, we have arranged them in two separate series, in circles of Period 6. This emphasizes their pairing (noticed long ago by Mendeleev and Klemm, and later by Shemyakin, Nekrasov, and Syrkin), which is due to the order in which the seven f places are filled. The lanthanide pairs have been allocated as suggested by Shemyakin [3] and Klemm, along the system radii III, IV, V, VI, VII, and VIII (2 pairs). The assignment of the Gd-Lu pair to Group III and of the Ce-Tb pair to Group IV is based upon their actually manifested maximum valency; the other pairs may be regarded as subgroups of Groups V-VIII (in accordance with their theoretical maximum valency, the coloring of their ions, and other regularities in their properties).

Group VIII of the elements consists of a main group (the inert gases) and a subsidiary metallic subgroup of Fe-Ru-Os. Group IX (the zero group) is eliminated, and Mendeleev's original octet of groups is re-established. In a broader sense, the "extra subgroups" (in H.A.Morozov's terminology [4]) of cobalt, nickel, and copper may also be assigned to Group VIII. The characteristic that is common to most of the elements in Group VIII (with the exception of Ru and Os) is the failure of the maximum observed positive valency to agree with the group number (in the table issued by the USSR Academy of Sciences on the centenary of Mendeleev's birth the iron, cobalt and nickel subgroups are considered to be subsidiary subgroups of Group VIII, with the inert gases as the major subgroup [5]).

In the proposed modernization of the table the copper subgroup constitutes a transitional group between Groups VIII and I; it may be regarded both as a subgroup of Group I (from the analogy of its electronic structure and the isomerism of its salts) and as a subgroup of Group VIII (from its maximum observed positive

valency of 3). This is in conformity with Mendeleev's own view of the copper subgroup.

The analysis of the degree of resemblance (analogy) between the elements within the groups and subgroups is of considerable importance both scientifically and pedagogically. Prof. B.V.Nekrasov, for instance, writes: "Thorough treatment of the periodic system is possible only when we make allowance for the structural features of atoms, not only in their neutral state, but also in all their typical valency stages" [6].

In the proposed modernization, this classification of the group elements into 3 subgroups is supplemented by graduations into seven qualitatively different kinds of analogies (homologies), represented graphically by different types of lines:

Complete analogies (in the atomic and ionic states), such as: Na–K–Rb–Cs–Fr.

Partial analogies (analogies in the atomic state, though not in the ionic state), such as: Na–Cu; Al–Ga.

Analogies only at the "characteristic" valency (corresponding to the group number), such as: S and Cr; Cl and Mn.

Analogies at valencies other than the characteristic one, such as: N and P; O and S; and F and Cl.

The cases of H–Li and He–Br, on the one hand, and of H–F and He–Ne, on the other, are two special types of analogy. The first of these types comprises elements that are related only as far as the physics of the atom is concerned, i.e., belonging to the same (s) family, but not related in the ionic state (Li^+ and Be^{++} as ions, and H^- and He^{++} as elementary particles); the second type consists of elements that are related solely in the physical properties of simple substances (or as negative ions, as in the case of H and F), but belong to different electronic families.

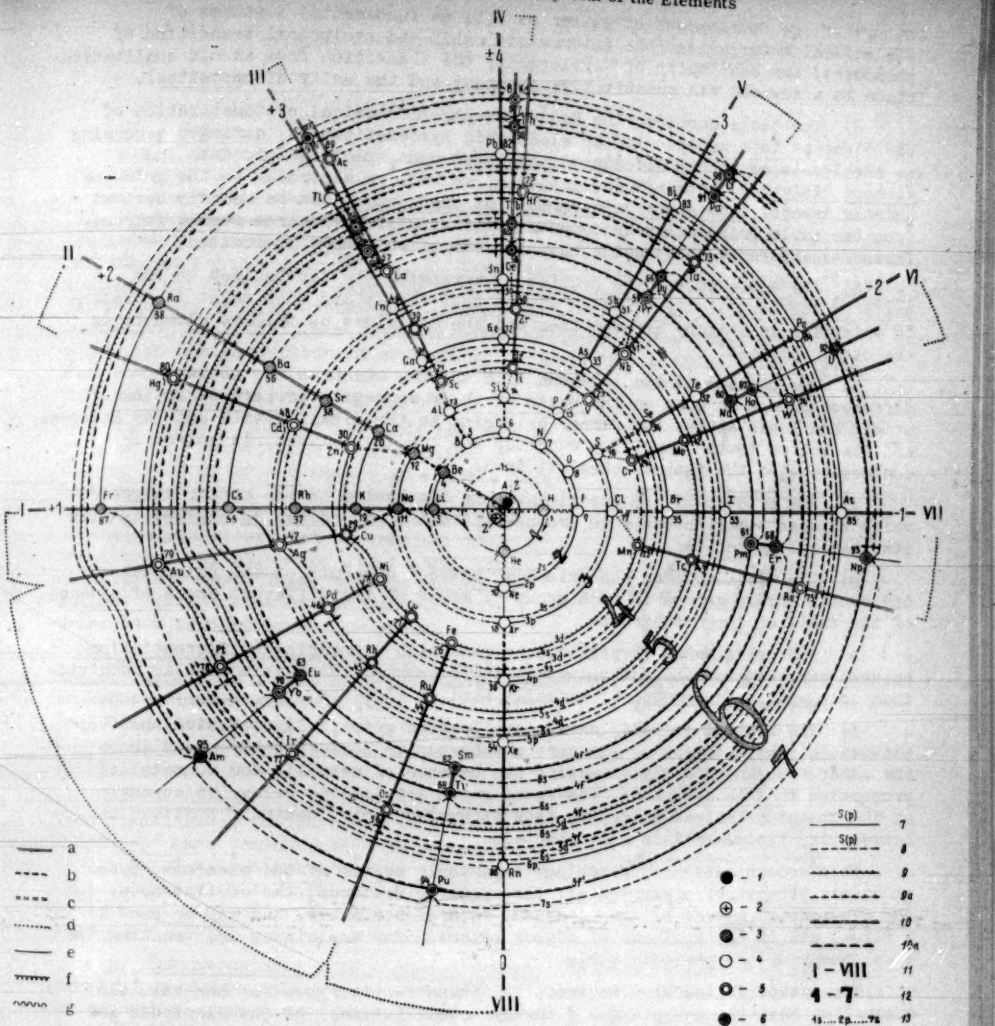
The table obviously permits of further extension of similar qualitative differentiation of the degree of resemblance. Thus, the Cr–Mo–W subgroup, established on the basis of complete analogies, may, like the elements of other subsidiary subgroups, be subdivided graphically into smaller subgroups: a) Cr–Mo, and b) W (based upon the difference in the number of unpaired electrons in the ground state, according to Syrkin).

5. Summing up, the author believes that the modernized Mendeleev periodic system of the elements possesses the following superiorities over the old classical form of the system.

a) The origin of the system from the development of the atom and the dialectical interrelationships of the whole (the atom and the system) and of the unit (the electron and the element) are clearly represented graphically. The nucleus, consisting of Z protons and (A - Z) neutrons for each element, is placed at the center of the "system-atom." Thus the cornerstone of the periodic law is represented graphically: the table does not contain two electrons that do not differ either in their orbits or in their different "place" in the orbit (both of their factors reflecting their differing energy states). The discreteness of the electrons' energy states results in discreteness of atomic structure and ultimately in the individuality of the elements and the discreteness of their properties (the influence of the constitution of the nucleus, which is, no doubt, negligible). This is the underlying idea of the table.

b) The following factors are clearly represented graphically: the spiral

D. I. Mendeleev's Periodic System of the Elements



1 - Neutron; 2 - proton; 3 - s-electrons (elements of the s family); 4 - p-electrons (elements of the p family); 5 - d electrons (elements of the d family); 6 - f electrons (elements of the f family); 7 - the s or p levels ("states") of the outer quantum shell (i. e., corresponding to the period number) are being completed; 8 - the s (or p) level is completed; 9 - the level d of the preceding quantum shell is being completed; 9a - the d level is completed; 10 - the f level of the preceding (third from the outside) quantum level is being completed; 10a - the f level is completed; 11 - groups of the periodic system; 12 - periods; 13 - electron quantum shells.

Types of element analogies:

a and b - Complete analogies in the atomic and ionic states

c - Incomplete analogies (analogies only in the atomic state).

d - Analogy only at the characteristic valency (corresponding to the group number)

e - Analogy at valencies other than the characteristic one.

f and g - Special kinds of analogy.

nature of the development of matter as well as fundamental features of dialectical materialism (the interrelationship and reciprocal transition of phenomena; the continuity of development; the transition from an old qualitative state to a new one via quantitative changes; and the unity of opposites).

c) The table combines the Mendeleev physicochemical systematization of the elements into groups with an electronic systematization, arranged according to the levels of electronic states, as based upon spectroscopic data and without violating the Mendeleev grouping, as well as according to the principal quantum layers. The electronic formula of any element can be readily derived from the table graphically by computing the completed electron shells (circumferences) crossed by the radius on which the given element is located.

d) The table solves the problem of arranging the lanthanides on the basis of the periodicity existing within that family and also makes it possible to establish an analogy between them and the actinides as well as elements in the other families.

e) The problem of the location of H and He, which belong to two different groups at once on the basis of their aggregate properties in the atomic and ionic state: the former belonging to the alkali metals and the halogens, and the latter to the beryllium subgroup and the inert gases, is solved in conformity with the factual chemical data.

f) The problem of the position within the system of the copper subgroup, which belongs simultaneously to Groups VIII and I, is solved in conformity with its chemical properties.

g) The table defines the "kinship" between elements of the principal and subsidiary subgroups in each group by means of the different angle of advance of the radii of these subgroups.

h) The table makes it possible to establish a graphical differentiation between various kinds of analogies between elements, which is needed to subdivide them into smaller subgroups of actually similar elements.

i) The typical (alkali) metals are located graphically opposite the typical non-metals (the halogens). The carbon subgroup is located between and above the other two, graphically stressing the balance of metallic and nonmetallic properties in this subgroup. The inert gases are located below, at an angle of 90° to the principal diameter, thus stressing their "neutral" position as between the typical metals and nonmetals.

This modernization of Mendeleev's periodic system of the elements, based on atomic structure, preserves all the specific features, the stellateness, and the dialectical nature of the classical form of the table, and may be used as a visual aid in institutions of higher learning for explaining and teaching the development of the periodic table.

The author is indebted to Prof. M.S.Skanavi-Grigoryeva for her valuable suggestion that the s - p - d - f energy levels (states) of the electrons and element families be represented in the table.

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TERNARY SYSTEMS WITH CLOSED LAYERING ISOTHERMS

I.L.Krupatkin

Closed layering isotherms have been found repeatedly in three-component systems with an upper ternary critical point [1]. The causes of their formation were disclosed in R.V.Mertslin's fundamental paper on this problem [1]. This paper derived a schema covering the formation of closed layering isotherms in a ternary system even when no upper ternary critical point is present, as represented in Fig. 1. Theprerequisites for this schema are as follows: the presence of layering with an upper critical solution temperature in one binary mapping system and of layering with a lower critical temperature in another, with the upper critical point being below the lower critical point; and the production of a chemical compound in the third binary system. When these conditions are satisfied, the isotherms located between the critical points will be closed ones.

The present paper deals with the problem of providing experimental confirmation of this schema. The water - phenol - phosphoric acid ternary system was used.[1] To learn whether the selected ternary system satisfied the schemaprerequisites, let us consider the physicochemical nature of its binary constituent systems. These systems are as follows phenol - water, phosphoric acid - water, and phosphoric acid - phenol.

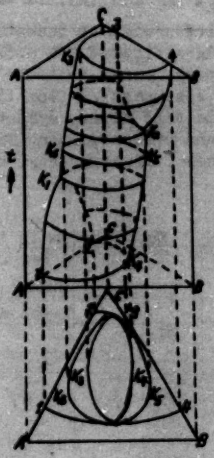

Fig. 1

1. The phenol - water system. In this system there is a stable layering region with an upper critical solution point at 68° [2]. Several authors have also investigated the conductance [3] and viscosity [4] of this system.

2. The phosphoric acid – water system. Investigations of the fusibility of this system [5] have demonstrated the presence within it of a chemical compound of phosphoric acid and water, viz: $H_3PO_4 \cdot 0.5\ H_2O$, with a melting point of 29°. The components of the system are miscible in all proportions in the liquid state.

3. The phosphoric acid - phenol system. We have investigated the equilibrium between the liquid phases in this system. As our researches, described below, have shown, this system exhibits a layering region with a lower critical solution temperature of 100°.

This discussion of the boundary binary systems indicates that two of them contain a layering region, one exhibiting an upper and the other a lower critical solution point, the lower critical solution point being 32° above the upper one. A chemical compound is formed in the third binary system, i.e., it is the

1) V.F.Ust-Kachkintsev did some research in this field [J. Gen. Chem. 7, 25 (1937)], but with a different objective in view.

predominant binary system in the given ternary system. Hence, the selected ternary system of water - phenol - phosphoric acid fully satisfies the prescribed conditions of the foregoing schema.

EXPERIMENTAL SECTION AND EVALUATION OF RESULTS

The following substances were employed in our research:

1. Phosphoric acid was available in the laboratory as an 85% solution. It was concentrated by the Erdmann method and then crystallized. The acid thus produced contained 99.98% H_3PO_4. The percentage of phosphoric acid was determined by titration.

2. The phenol was distilled, the fraction boiling at 182° being collected; its melting point was 42°.

3. Double-distilled water was used.

Several points were plotted in the phenol - water and phosphoric acid - water systems by way of checking our reagents. The results were in good agreement with the figures given in the literature. The research was carried out by Alekseev's method [2], in sealed ampoules immersed in an oil thermostat.

We began with an investigation of the phosphoric acid - phenol system. Then we investigated the phosphoric acid - phenol - water ternary system by passing polythermal sections through its prism, two kinds of sections being studied: some passing from the phenol vertex to the face of the water - phosphoric acid binary system at 5, 10, 20, 30, 50, 70, 85, and 95% of the latter; and others passing from the water vertex to the face of the phosphoric acid - phenol binary system at 21, 35, 50 and 65% of the latter.

TABLE 1

Equilibrium in the Phosphoric Acid - Phenol System

No	t°	Per cent phosphoric acid by weight		Remarks
		Layer A	Layer B	
1	100.5	32.00		Critical point
2	101.0	29.12	35.08	Critical turbidity 93°
3	101.5	-	37.56	
4	103.5	23.67	-	Critical turbidity 95°
5	104.0	-	42.07	
6	106.5	19.95	-	Critical turbidity 97°
7	108.5	-	50.46	
8	114.0	-	60.45	
9	115.0	15.39	-	Critical turbidity 103°
10	118.0	-	70.85	
11	121.5	-	80.36	Tarring set in at a higher temperature
12	129.0	10.14	-	Critical turbidity 119°

The numerical findings on the phosphoric acid - phenol binary system are listed in Table 1. The curve giving the equilibrium between the liquid phases, plotted from the experimental data, is reproduced in Fig. 2. The area outlined by the dashed line is the region in which a critical turbidity exists. As the figure shows, the phosphoric acid - phenol system is one of those possessing a lower critical solution point. As a matter of fact, the curve of equilibrium between the liquid phases exhibits a lower critical point (an Alekseev point [7]) at 32% of phosphoric acid and 68% of phenol and at 100

It is thrown off toward the phenol corner. The solubility of phenol in phosphoric acid and of phosphoric acid in phenol diminishes as the temperature is raised, the solubility of phenol in phosphoric acid being much higher than that of phosphoric acid in phenol between 100 and 130°. The two solubilities nearly level out as 130° is approached, coming within 10% of each other. The effect of temperature upon the solubility of phosphoric acid in phenol increases as the temperature drops. That is why the solubility curve of phosphoric acid in phenol drops steeply at high temperatures and is much flatter at lower temperatures. The effect of temperature upon the solubility of phenol in phosphoric acid is qualitatively the same, though the quantitative picture is wholly different. In this case the flat section of the curve is very long, extending over more than 40%, so that the solubility of phenol in phosphoric acid is very high in the 100-120° range, the lower critical solution point being thrown off toward the phenol corner. A change occurs in the components in the vicinity of the phosphoric acid corner, the liquid turning black, thus making it impossible to plot the curve in this region of the diagram. As we see from the graph, the region of critical turbidity is rather large, extending from the critical point leftward to the phenol corner.

The numerical data secured in our investigations of the polythermal sections through the phosphoric acid - phenol - water ternary system are listed in Tables 2 - 9. It should be noted that the section at 95% phosphoric acid has been traced only near the vertex, where the polytherm is a vertical line dropping to 3% phenol. The polytherms of these sections are reproduced in Fig. 3, in which the liquid phase equilibrium curve for the phenol - water binary system is plotted for the sake of comparison.

TABLE 2

Section at 5% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	41.0	7.57	-
2	49.0	-	86.80
3	57.5	9.96	-
4	75.0	-	84.91
5	79.0	19.79	-
6	84.0	27.11	-
7	87.0	39.17	-
8	90.0	56.06	-
9	92.0	-	81.35
10	92.5	70.66	-
11	94.5	75.05	-
12	95.0	-	78.76

TABLE 3

Section at 10% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	23.0	-	94.71
2	49.0	7.15	-
3	64.0	-	91.21
4	76.0	11.20	-
5	88.0	15.56	-
6	97.0	24.80	-
7	102.0	34.96	-
8	108.0	45.32	-
9	110.0	-	85.97
10	114.5	54.48	-
11	125.0	63.92	-
12	129.0	74.05	-
13	130.0	-	81.35

The sections extending from the water vertex to the side of the phenol - phosphoric acid binary system were investigated only in the vicinity of that side. They are reproduced in Fig. 4. The experimental polytherms were used in plotting the derived isothermal sections: at 60°, i.e., at a temperature below the critical one in the phenol - water binary system; at 85°, i.e., at a temperature between the upper and lower critical points in the boundary binary systems; and at 120°, i.e., at a temperature above the critical in the phenol - phosphoric acid binary system. The resultant isotherms are plotted in Fig. 5.

TABLE 4

Section at 20% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	44.0	5.60	-
2	50.0	-	94.50
3	74.0	6.73	-
4	80.0	-	93.53
5	94.0	9.53	-
6	107.5	13.31	-
7	109.0	-	90.78
8	117.5	-	89.46
9	123.0	20.23	-

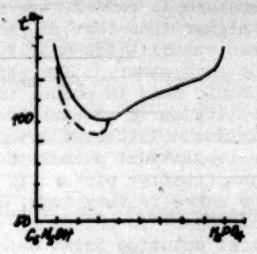

Fig. 2.

TABLE 5

Section at 30% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	39.0	3.26	-
2	60.0	-	95.18
3	69.0	4.51	-
4	78.0	5.11	-
5	81.0	-	94.46
6	102.0	7.34	93.15
7	116.0	-	91.54
8	122.0	9.92	-

TABLE 6

Section at 50% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	49.0	2.33	-
2	52.0	-	96.02
3	80.0	-	95.59
4	92.0	3.28	-
5	98.0	-	94.72
6	110.0	4.04	-
7	117.0	-	93.52
8	126.0	5.53	-

TABLE 7

Section at 70% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	56.0	-	96.04
2	71.0	2.03	-
3	74.0	-	95.77
4	90.0	-	95.51
5	99.0	2.48	-
6	114.0	3.11	-
7	123.0	3.60	-
8	128.0	-	94.87

TABLE 8

Section at 85% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	55.0	-	95.98
2	72.0	1.96	95.46
3	93.0	2.35	-
4	110.0	-	94.59
5	115.0	2.74	-
6	120.0	3.04	-
7	130.0	-	94.03

The numerical data indicate that the solubility of water in mixtures of phosphoric acid and phenol is negligible, of the order of 1%, the solubility dropping still lower as the temperature is raised and becoming practically independent of the composition of the mixture. The solubility of phosphoric acid - phenol mixture in water, on the other hand, is fairly high, increasing with rising temperature. The solubility of a phosphoric acid - water mixture in phenol is only slightly affected by temperature, but varies sharply with the concentration of phosphoric acid in the solutions. In strong solutions of phosphoric acid the solubility is low, of the order of 5%, rising sharply,

TABLE 9

Sections Passing from the Water Vertex to the Side of the Phenol - Phosphoric Acid Binary System

Section	t°	% water by weight
Section at 21.35% phenol	121.0	0.00
	90.0	0.72
	67.0	1.24
Section at 50.00% phenol	108.5	0.00
	85.0	0.50
	68.0	0.85
Section at 65.00% phenol	101.0	0.00
	80.0	0.40
	62.0	0.74

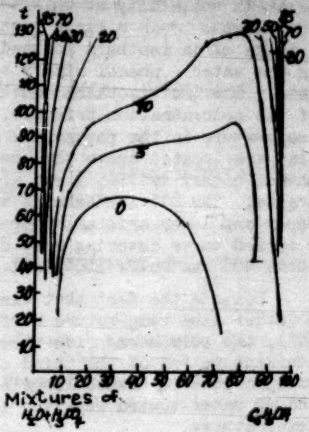

Fig. 3.

however, as the acid concentration drops, finally reaching complete miscibility. The solubility of phenol in phosphoric acid solutions likewise depends upon the concentration of the latter. In strong phosphoric acid solutions, say up to 40%, the phenol's solubility remains constant at about 5%, and is only slightly affected by the temperature. As the concentration of phosphoric acid falls below 40%, the phenol's solubility rises substantially. This increase in solubility likewise rises with rising temperature, reaching miscibility in all proportions. The decrease in the solubility of the phenol as the phosphoric acid concentration rises fully agrees with the theory of the origin of closed layering isotherms in ternary systems, since it is precisely at high concentrations of phosphoric acid in aqueous solutions that it forms a hydrate with the water.

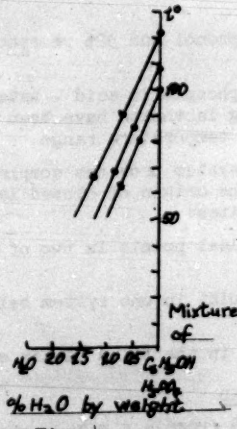

Fig. 4.

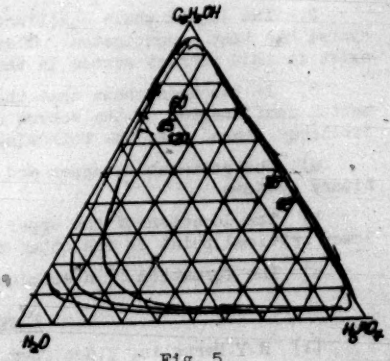

Fig. 5.

The 60° isotherm constitutes a layering region that starts at the break in solubility at this temperature in phenol - water binary system and extends over a large part of the concentration triangle. It is an example of an isotherm located below 68°, i.e., below the critical point in the water - phenol binary system, since all such isotherms will look like this. The 120° isotherm constitutes a layering region extending over much of the concentration triangle, from the solubility discontinuity at this temperature in the phosphoric acid - phenol binary system. All the isotherms that are located above the lower critical temperature in the phosphoric acid - phenol binary system, i.e., above 100°, will exhibit the same qualitative traits. The 85° isotherm is an example of an isotherm lying between the upper and lower critical temperatures in the boundary binary systems. It is a closed curve covering most of the concentration triangle. All isotherms above 68° and below 100° will also be closed curves of this sort.

Despite the fact that the upper and lower critical points are so close together (the temperature difference between them being slightly more than 30°), the polytherms rise steeply upward. This may explain the poor homogenizing action of the third components in binary layering, namely, of phosphoric acid toward layering in the phenol - water system at low temperatures, and of water toward layering in the phosphoric acid - phenol system at high temperatures.

Thus, the results of our research on the phenol - water - phosphoric acid ternary system indicate that closed layering isotherms exist in this system at temperatures that lie between the upper and lower critical points in the water - phenol and phenol - phosphoric acid systems, respectively, with a chemical compound existent in the phosphoric acid - water system. This is full experimental confirmation of the schema cited above for the origin of layering isotherms in ternary systems, provided the upper critical temperature is one of the boundary binary systems is lower than the lower critical temperature in another system and that the third system exhibits a chemical compound.

SUMMARY

1. The liquid phase equilibrium in the phenol - phosphoric acid system has been investigated. A stable layering region, with a lower critical solution temperature, has been found.

This lower critical point occurs at 68% phenol and 32% phosphoric acid and at a temperature of 100°.

2. The liquid phase equilibrium in the phosphoric acid - water - phenol system has been investigated. Closed layering isotherms have been found to exist in this ternary system in the 68 - 100° temperature range.

3. It has been shown that this ternary system provides complete experimental confirmation of the schema cited for the origin of closed layering isotherms, based upon the following prerequisites:

a) The presence of upper and lower critical points in two of the binary systems.

b) The location of the upper critical point in one system below the lower critical point in the other system.

c) The formation of a chemical compound in the third binary system.

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THE N-ARYL AMIDES OF HYDROXY CARBOXYLIC ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

XI. THE INTRAMOLECULAR CONDENSATION OF ARYL AMIDES OF 2,2'-DIMETHOXYBENZILIC ACID

P.A. Petunin

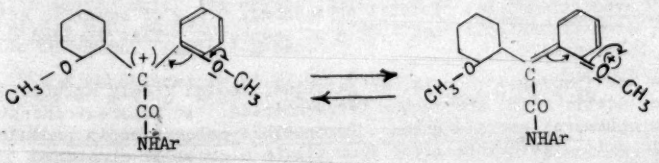
As we have already observed, the introduction of an alkoxy group into an aryl attached to a carbinol carbon atom greatly increases the basic properties of aryl amides of hydroxy carboxylic acids and deepens the color of the cations of their onium salts [1]. In this connection we were interested in determining the effect of these changes upon the rate of intramolecular condensation; we did this by determining the condensation rate of the o-aniside of 2,2'-dimethoxybenzilic acid. Our results are listed in Table 1. The figures cited indicate that the condensation rate is not diminished despite the appreciable increase in the basicity of the aryl amides of 2,2'-dimethoxybenzilic acid (the addition of 70% sulfuric acid yields a halochromic salt) and the deeper color of their halochromic salts (emerald-green). This means that the condensation rate does not depend upon the strength of the bond between the acid anion and the organic cation, but is governed by the internal structure of the cation, as we have shown in condensing aryl amides with 4,4'-dimethoxybenzilic acid [2]. The higher rate of condensation and the lower basicity of the aryl amides of 2,2'-dimethoxybenzilic acid, compared to the aryl amides of 4,4'-dimethoxybenzilic acid, may be explained by the manifestation of a steric effect, caused by the presence of methoxy groups in the ortho position to the central carbon atom.

TABLE 1

Test No.	Bath Temperature, °C	Time required for color to disappear		
		$ArNHCOC(OH)Ar_2'$	$ArNHCOC(OH)Ar_2''$	$ArNHCOC(OH)Ar_2'''$
1	10°	53'30"	57'	3'30"
2	20	21'10"	26'	2'
3	30	10'26"	11'	1'
4	40	6'10"	5'	0'35"

Ar' = $o\text{-}CH_3OC_6H_4-$; Ar'' = $p\text{-}CH_3C_6H_4-$; Ar''' = C_6H_5-.

As we know, steric factors can exert an appreciable effect upon conjugation [3]. The structure of the cation of a halochromic salt of an aryl amide of 2,2'-dimethoxybenzilic acid may be represented as follows:



(I) (II)

The steric effect interferes with the arrangement of the central carbon atom and the oxygen of the methoxy group in the same plane as the benzene ring. This diminishes the extent of the displacement of the unshared electron pair of the methoxy oxygen atom and sets up more favorable conditions for a cation structure with a reactive center at the carbinol carbon atom (I). Inasmuch as the cation structure with an electron gap at the central carbon atom (I) is of importance in condensation, the condensation rate of aryl amides of 2,2'-dimethoxybenzilic acid should be higher, and their basic properties should be less pronounced, than in the aryl amides of 4,4'-dimethoxybenzilic acid.

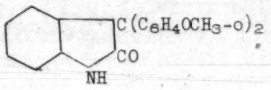
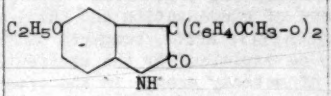
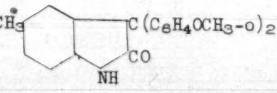
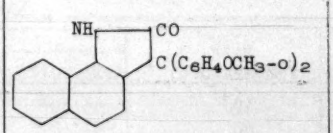
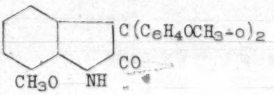
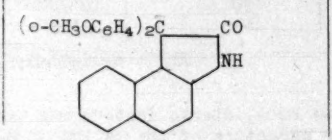
We performed the following condensation:

$$ArNHCOC(OH)(C_6H_4OCH_3\text{-}o)_2,$$

where: Ar = C_6H_4–, o-$CH_3OC_6H_4$–, α-$C_{10}H_7$– and β-$C_{10}H_7$–

to prepare the required reagents. The properties of the resulting compounds are listed in Table 2. Since the aryl amides of 2,2'-dimethoxybenzilic acid form halochromic salts with 70% sulfuric acid, we tested their condensation with dilute sulfuric acid. In every case we secured a halochromic compound, the aryl amides entering into the condensation reaction. This bears out our earlier conjecture that water is not split off directly during condensation, the reaction involving a stage in which a halochromic salt is formed.

TABLE 2

No	Formula	M.p.	No	Formula	M.p.
1		196	4		208.5-209.5
2		219-220	5		263
3		230-231	6		301-303

EXPERIMENTAL

2,2'-Dimethoxybenzilanilide. Initial substances: 6.4 g of oxanilic ester, 38.8 g (5 moles) of o-iodoanisole, and 4.05 g of magnesium. This yielded 8.1 g or 67.2% of the theoretical.

The anilide was insoluble in water or gasoline, though freely soluble in alcohol, benzene, acetic acid, and carbon tetrachloride. It colored concentrated sulfuric acid an ephemeral emerald-green. Perceptible coloration is produced with 70% sulfuric acid. It crystallized from dilute alcohol in clustered needles, m.p. 142°.

0.4312 g substance: 11.07 ml 0.1 N. H_2SO_4. 0.2138 g substance: 5.8 ml 0.1 N H_2SO_4. Found %: N 3.59, 3.79. $C_{22}H_{21}O_4N$. Calculated %: N 3.86.

2,2'-Dimethoxybenzil-p-toluide. This was prepared from 6.4 g (1 mole) of p-tolyloxanilic ester, 33 g of o-iodoanisole (4.5 moles), and 3.4 g of magnesium. The yield was 6.7 g or 57.7% of the theoretical.

The toluide dissolved in sulfuric acid, coloring it an ephemeral emerald-green. It crystallized from dilute alcohol as needles with a m.p. of 153°.

0.3102 g substance: 8.39 ml 0.1 N. H_2SO_4. 0.2202 g substance: 6.1 ml 0.1 N H_2SO_4. Found %: N 3.79, 3.88. $C_{23}H_{23}O_4N$. Calculated %: N 3.71.

2,2'-Dimethoxybenzil-o-aniside. Initial substances: 7.4 g (1 mole) of o-methoxyoxanilic ester, 38.8 g of o-iodoanisole, and 5.05 g of magnesium. The yield was 8 g, or 62% of the theoretical. It crystallized from dilute alcohol; m.p. 151-152°. The aniside colored sulfuric acid an ephemeral emerald-green.

0.4145 g substance: 10.75 ml 0.1 N. H_2SO_4. 0.2373 g substance: 6.4 ml 0.1 N. H_2SO_4. Found %: N 3.63, 3.78. $C_{23}H_{23}O_5N$. Calculated %: 3.56.

2,2'-Dimethoxybenzil-p-phenetide. Initial substances: 5.9 g (1 mole) of p-ethoxyoxanilic ester, 29.1 g of o-iodoanisole, and 3.04 g of magnesium. The yield was 8 g, or 79.2% of the theoretical.

The phenetide was insoluble in water or ether, though freely soluble in most of the other common organic solvents. It dissolved in sulfuric acid, producing an emerald-green coloration that vanished completely after standing for a short time. It crystallized from dilute acetic acid as colorless rosettes with a m.p. of 178-179°.

0.4136 g substance: 10.75 ml 0.1 N. H_2SO_4. 0.3308 g substance; 8.4 ml 0.1 N. H_2SO_4. Found %: N 3.64, 3.55. $C_{24}H_{25}O_5N$. Calculated %: N 3.44.

2,2'-Dimethoxybenzil-α-naphthalide. This was prepared by reacting 6.1 g of α-naphthyloxaminic ester with o-iodoanisole magnesium, prepared from 9.1 g of o-iodoanisole and 3.04 g of magnesium. The yield was 5 g, or 49% of the theoretical.

The napthalide was insoluble in water or gasoline, slightly soluble in alcohol, and freely soluble in ether and benzene. It colored conc.sulfuric acid an ephemeral green. It crystallized from a small quantity of benzene as minute crystals with a m.p. of 157-158°.

0.5768 g substance: 14.1 ml 0.1 N. H_2SO_4. 0.2430 g substance: 6.2 ml 0.1 N. H_2SO_4. Found %: N 3.42, 3.57. $C_{26}H_{23}O_4N$. Calculated %: N 3.39.

2,2'-Dimethoxybenzil-β-naphthalide. Initial substances: 6.1 g of β-naphthyloxaminic ester, 29.1 g of o-iodoanisole, and 3.04 g of magnesium. The yield was 6.4 g or 62.7% of the theoretical.

The naphthalide was slightly soluble in alcohol and benzene and readily soluble in acetic acid. It crystallized from dilute acetic acid as colorless prisms with a m.p. of 172-173°. It dissolved in sulfuric acid, coloring the latter an ephemeral emerald-green.

0.5548 g substance: 14.25 ml 0.1 N. H_2SO_4. 0.2219 g substance: 5.4 ml 0.1 N H_2SO_4. Found %: N 3.59, 3.41. $C_{26}H_{23}O_4N$. Calculated %: N 3.39.

3,3-Bis-(2-methoxyphenyl)-oxindole. (o-Dianisolisatin). 5 ml of 75% sulfuric acid were added to a solution of 0.5 g of 2,2'-dimethoxybenzilanilide in 5 ml of glacial acetic acid. The emerald-green color produced by dilute sulfuric

acid vanished rapidly. The yield was 0.4 g, or 84% of the theoretical. Crystallization from dilute acetic acid yielded colorless rhombohedra with a m.p. of 196°.

o-Dianisolisatin has been synthesized by us for the first time.

0.1117 g substance: 0.3130 g CO_2; 0.0559 g H_2O; 0.3280 g substance: 9.1 ml 0.1 N H_2SO_4. Found %: C 76 46; H 5.6; N 3.88; $C_{22}H_{19}O_3N$. Calculated %: C 76.52; H 5.51; N 4.06.

3,3-Bis-(2-methoxyphenyl)-5-methyloxindole. 3,3-Bis-(2-methoxyphenyl)-5-methyloxindole was synthesized by adding conc. sulfuric acid to an acetic acid solution of 2,2'-di-methoxybenzil-p-toluide. The end of the reaction was indicated by the disappearance of the emderald-green coloration. The yield of the reaction product was 87.7% of the theoretical. The substance was insoluble in water, slighly soluble in gasoline, and freely soluble in alcohol, acetic acid, benzene toluene, and chloroform. It crystallized from dilute acetic acid as colorless needles gathered in little sheaves, with a m.p. of 219-220°.

0.2436 g substance: 7.27 ml 0.1 N H_2SO_4. 0.2679 g substance: 8 ml 0.1 N H_2SO_4. Found %: N 4.14, 4.18. $C_{23}H_{21}O_3N$. Calculated %: N 3.9.

3,3-Bis-(2-methoxyphenyl)-7-methoxyoxindole. Initial substances: a solution of 0.5 g of 2,2'-dimethoxybenzil-o-aniside in 5 ml of acetic acid and 5 ml of 75% sulfuric acid. After the emerald-green coloration had disappeared, the reaction mass was carefully diluted with water until slight cloudiness resulted and then set aside to stand until crystallization set in. Colorless parallelograms with a m.p. of 230-231°. The yield was 0.4 g, or 87% of the theoretical.

0.4530 g substance: 11.9 ml 0.1 N H_2SO_4. 0.3100 g substance: 7.8 ml 0.1 N H_2SO_4. Found %: N 3.68, 3.52. $C_{23}H_{21}O_4N$. Calculated %: N 3.73.

3,3-Bis-(2-methoxyphenyl)-5-ethoxyoxindole was synthesized by adding conc. sulfuric acid to an acetic acid solution of 2,2'-dimethoxybenzil-p-phenetide, the yield approximating 100%. Crystallization from dilute acetic acid yielded colorless hexagonal lamellae with a m.p. of 208.5 - 209.5°.

0.4492 g substance: 12.26 ml 0.1 N H_2SO_4. 0.3360 g substance: 9 ml 0.1 N H_2SO_4. Found %: N 3.6, 3.75. $C_{24}H_{23}O_4N$. Calculated %: N 3.6.

3,3-Bis-(2-methoxyphenyl)-6,7-benzooxindole. [3,3-Bis-2-methoxyphenyl)-α-naphthoxindole]. This was synthesized by condensing 2,2'-dimethoxybenzil-α-naphthalide, the yield approximating 100%. It crystallized from dilute acetic acid as colorless needles gathered into clusters, m.p. 263°.

0.3990 g substance: 10.8 ml 0.1 N H_2SO_4. 0.3602 g substance: 9.5 ml 0.1 N H_2SO_4. Found %: N 3.78, 3.69. $C_{26}H_{21}O_3N$. Calculated %: N 3.54.

3,3-Bis-(2-methoxyphenyl)-4,5-benzooxindole. [3,3-Bis-(2-methoxyphenyl)-β-naphthoxindole]. Condensation of the β-naphthalide of 2,2'-dimethoxybenzilic acid using sulfuric acid yielded 83.6% of 3,3-bis-(2-methoxyphenyl)-β-naphthoxindole. Colorless clusters (from dilute acetic acid) with a m.p. of 301-303° (with decomposition).

0.3348 g substance: 8.9 ml 0.1 N H_2SO_4. 0.3458 g substance: 9 ml 0.1 N H_2SO_4 Found %: N 3.72, 3.64. $C_{26}H_{21}O_3N$. Caculated %: N 3.54.

SUMMARY

1. A method has been developed for synthesizing o-dianisolisatin and its derivatives. Several compounds not described in the literature have been synthesized and their properties investigated.

2. Condensation of aryl amides of 2,2'-dimethoxybenzilic acid has been used to show that there is no hard-and-fast relationship between the increase in the basicity of the aryl amides and the deepening of the color of their halochromic salts on the one hand and the rate of their intramolecular condensation on the other.

3. The aryl amides of 2,2'-dimethoxybenzilic acid have been used to show the influence of the steric effect, due to the presence of methoxy groups in ortho positions to the carbinol carbon atom upon the rate of intramolecular condensation and upon the basic properties of the aryl amides. An explanation is furnished for this phenomenon.

4. Several aryl amides of 2,2'-dimethoxybenzilic acid, not described in the literature, have been synthesized and their properties investigated.

LITERATURE CITED

[1] P.A.Petyunin, J. Gen. Chem. 21, 2193 (1951). [1)]

[2] P.A.Petyunin, J. Gen. Chem. 22, 296 (1952). [2)]

[3] A.I.Titov, J. Gen. Chem. 16, 1893 (1946).

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Received April 18, 1950.

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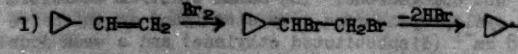
1) See Consultants Bureau English translation, p. 2449.

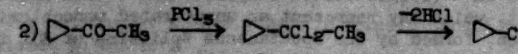
2) See Consultants Bureau English translation, p. 359.

CYCLOPROPYLACETYLENE

Ya. M. Slobodin and I. N. Shokhor

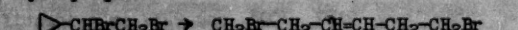
Cyclopropylacetylene has not been previously described. The following two reactions have been employed in the present research to synthesize it:





In the first of these methods, the initial substance is vinylcyclopropane, prepared by Demyanov's method [1,2]. Brominating the latter yielded the dibromide, which Demyanov took to be the individual dibromide of vinylcyclopropane. We identified this dibromide spectroscopically. Its Raman spectrum exhibited the frequencies of 752, 826, 884, 1025, 1196, 1435, 3016, and 3080 cm^{-1} belonging to a three-membered ring. The dibromide spectrum likewise exhibited a double-bond line with a frequency of 1664 cm^{-1} and average intensity, as well as the C–Br bond frequencies of 568, 598, 623, 658, and 678 cm^{-1}, which apply to both the $=CBr$ and the $-CH_2Br$.

The double-bond frequency of 1664 cm^{-1} is characteristic of disubstituted ethylene, which may be formed as the result of the partial opening of the three-membered ring in a manner similar to that cited in our report [3] for α-bromoethylcyclopropane:



The formation of a dibromide of this structure agrees with Demyanov's findings; he obtained a tetrabromide with the structure of $CH_2Br–CH_2–CHBr–CHBr–CH_2Br$ by reacting the dibromide of vinylcyclopropane with bromine.

The ratio of the bromide with a three-membered ring and the unsaturated dibromide is 3:2.

Hence, the dibromide of vinylcyclopropane described by Demyanov is a mixture of two substances.

Using sodium amide to split HBr out of the dibromide [4] yielded a very low yield of cyclopropylacetylene, the principal product being an undistillable gummy mass.

Reacting the dibromide with KOH in the monoethyl ether of ethylene glycol [5] at 140-160° raised the yield of the hydrocarbon to 94%, based on the cyclic bromide.

Spectroscopic and chemical analysis of the hydrocarbon indicated that it was pure cyclopropylacetylene. The hydrocarbon's boiling point was 52.2 - 52.6° at 750 mm; d_4^{20} 0.7828, n_D^{20} 1.4284.

Raman spectrum: 207(10broad), 488(4), 583(1), 608(1), 752(5), 811(1), 875(3), 938(8), 1005(1), 1033(1), 1187(10), 1351(8), 1453(4broad), 2120(10), 3024(5broad), 3085(4).

The frequency of 2120 cm^{-1} identifies the hydrocarbon as a monosubstituted

acetylene. The frequencies of 752, 811, 875, 1033, 1187, 1453, 3024 and 3085 cm^{-1} apply to a three-membered ring.

The hydrocarbon produces the characteristic precipitates of a monosubstitution derivative of acetylene with various reagents.

Ozonolysis of the hydrocarbon yielded only formic and cyclopropylformic acids.

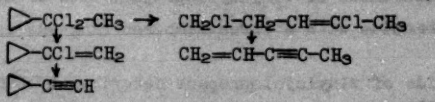
To synthesize cyclopropylacetylene by Reaction (2) acetylcyclopropane was treated with PCl_5 [6]. Spectroscopic analysis of the resultant dichloride indicated that it was not homogeneous. The Raman spectrum exhibited the 1187 cm^{-1} frequency of the cyclopropane ring. We also found an intensive double-bond frequency of 1668 cm^{-1} (disubstituted ethylene) and a weak double-bond frequency of 1640 cm^{-1}, which may represent an unsaturated monochloride of the cyclopropane series, formed by the spontaneous splitting of HCl from the dichloride [7]. Analysis of the dichloride for chlorine yielded a lower percentage than called for theoretically. The C–Cl bond frequencies of 578, 618, 658, 693, and 713 cm^{-1} confirm the presence of the chlorine atom at both the primary carbon atom and at the more highly substituted carbon atoms.

When we split the hydrohalide out of the mixture of dichlorides, we secured a hydrocarbon mixture, the intensity of the acetylene-bond frequencies indicating that the percentage of cyclopropylacetylene in the mixture might be estimated as 30%.

The Raman spectrum exhibited all the frequencies of cyclopropylacetylene. Moreover, we found two double-bond frequencies (a weak frequency of 1586 cm^{-1} and an intensive one of 1609 cm^{-1}). Three acetylene-bond frequencies were found, one weak frequency of 2098 cm^{-1} and two others of 2189 and 2237 cm^{-1}, the last frequency being an intensive one.

The frequencies of 1586, 1609, 2187, 2098, and 2237 cm^{-1} identify the conjugation of the α-ethylene and the α-acetylene bonds, so that the only possible structure in this case of ours was: $CH_3-C\equiv C-CH=CH_2$.

The formation of all the hydrocarbons specified may be represented as follows:



In Report [3] we noted that the presence of a single chlorine atom at the carbon atom linked to the three-membered ring causes a slight cleavage of the ring. The data cited in the present report indicate that an increase in the number of chlorine atoms attached to the carbon atom linked to the three-membered ring produces a greater cleavage of the ring.

I.A. Dyakonov [6], who was the first to investigate the reaction of PCl_5 with acetylcyclopropane, conjectured that this involved the complete rupture of the three-membered ring. Our spectroscopic analysis has shown that the cyclopropane ring is retained in part during this process.

EXPERIMENTAL

Vinylcyclopropane bromide. The original vinylcyclopropane was prepared by the Demyanov method [1]. Bromine was slowly added from a dropping funnel to 3.4 g of the hydrocarbon, dissolved in 50 ml of anhydrous ether and chilled to within −10 to −15°, until the bromine coloring no longer disappeared. Nearly

the calculated quantity of bromine was consumed in this bromination. The ether solution was washed with water, then with a soda solution, and again with water, after which it was separated and desiccated with calcium chloride. Driving off the ether left behind the nearly colorless bromide, which was distilled at a vacuum of 35 mm. Almost all of it distilled at 110-112°, a negligible residue being left in the flask. The yield of the bromide was 9.6 g, or 83% of the theoretical. At 10 mm the bromide distilled at 79 - 81°.

d_4^{20} 1.8022 (according to Demyanov, d_4^{15} 1.818); n_D^{20} 1.53802; MR_D 39.75; Calc. 38.62.

The exaltation of 1.07 was somewhat higher than the increment for the trimethylene ring.

0.4647 g substance: 0.7644 g AgBr (Carius). Found %: Br 70.00. $C_5H_8Br_2$. Calculated %: Br 70.18.

Determination of the degree of unsaturation by means of the bromine number is undependable, since bromine is added and the trimethylene ring ruptured even in the dark. Hence, the results depend upon the time of contact with the bromine solution. Direct titration of a weak bromine solution yielded the following results: 0.7 ml of a 0.1 molar solution of bromine in CCl_4 was added to 0.4703 g of the bromide, which is equivalent to a content of 37% of the unsaturated bromide.

Raman spectrum of the bromide: 145(3), 166(2), 192(8), 300(3), 325(8), 407(1), 448(2), 538(2), 568(5), 598(8), 623(3), 658(5), 678(10), 752(5), 801(3), 826(3), 855(1), 884(5), 914(5), 933(5), 1025(3), 1053(4), 1111(3), 1144(3), 1196(8), 1234(6), 1295(3), 1351(1), 1398(4), 1435(5), 1462(5), 1664(4), 2872(2), 2921(2), 2961(6), 3016(6), 3080(5).

A comparison of the intensity of the trimethylene ring frequencies with those of the double bond indicates that the percentage of the unsaturated bromide is approximately 40%, which agrees satisfactorily with the results of bromine titration.

Cyclopropylacetylene. Vinylcyclopropane bromide (21 g) was slowly added from a dropping funnel to a solution of 25 g of KOH in 140 ml of ethyl cellosolve, heated to boiling. The vapors of the low-boiling reaction products passed through the reflux condenser, warmed with water at a temperature of 60°, without condensing. The hydrocarbon condensed in a well-chilled coil and was collected in a receiver chilled to -20°. The hydrocarbon yield was 3.5 g, or 94%, based on the percentage of a product with a three-membered ring in the dibromide. The hydrocarbon was desiccated with calcium chloride. It distilled completely at 52.2 - 52.6° at 750 mm. A test for halogens was negative. The hydrocarbon was colored yellowish-green by tetranitromethane. It reacted quantitatively with Behal's reagent, producing a voluminous white precipitate. Ammoniacal cuprous chloride threw down a yellow precipitate. The silver derivative detonated when heated.

d_4^{20} 0.7828; n_D^{20} 1.4284. Found MR_D 21.71. C_5H_6 . Calculated MR_D 21.73 (the increment of a three-membered ring being taken as 0.7).

0.1054 g substance: 0.3503 g CO_2; 0.0867 g H_2O. Found %: C 90.70; H 9.21. C_5H_8. Calculated %: C 90.91; H 9.09.

The Raman spectrum is given above.

0.7 g of the hydrocarbon was ozonated in a chloroform solution chilled with dry ice. The ozonide was decomposed with water. The reaction products

were heated with an excess of silver oxide on a boiling water bath. The silver salts were dissolved in a large amount of water and then heated on a boiling water bath until the silver formate decomposed completely. The residual silver salts were concentrated to small volume in vacuo. The colorless crystals that settled out were squeezed out on a porcelain plate, kept in a desiccator over sulfuric acid, and then analyzed.

0.0477 g substance: 0.0266 g Ag. Found %: Ag: 55.77. $C_4H_5O_2Ag$. Calculated %: Ag 55.95.

α,α-Dichloroethylcyclopropane. Methyl cyclopropyl ketone, with a b.p. of 111-112.5°, prepared from acetopropyl alcohol [8,9], was treated with PCl_5, 20 g of the ketone being slowly added to a flask containing 55 g of phosphorus pentachloride, chilled with ice water. After the ketone had been added, the mixture was allowed to stand for 1 hour at room temperature and then poured out into ice water. The dichloride was extracted with ether, washed with water, and desiccated with calcium chloride. Driving off the ether yielded 21 g of the crude chloride, or 64% of the theoretical. Distilling the crude product at 85 mm yielded the following fractions: 1) 64 - 66°: 3.5 g; 2) 67 - 91°: 7 g; and 3) 91 - 94°: 9 g; the flask residue weighed 1.5 g. The 64 - 66° fraction contained some of the original ketone (reaction with 2,4-dinitrophenylhydrazine). The intermediate fraction was a mixture of the dichloride and the unsaturated monochloride, formed by the splitting off of hydrogen chloride. The 91 - 94° fraction consisted chiefly of the cyclic dichloride, with a trace of the unsaturated dichloride, formed as the result of the cleavage of the three-membered ring.

d_4^{20} 1.1256; n_D^{20} 1.4680; MR_D 34.33; Calc. 34.54.

0.0474 g substance: 0.0938 g AgCl (Carius). Found %: Cl 48.95. $C_5H_8Cl_2$. Calculated %: Cl 51.08.

Raman spectrum of the fraction with a b.p. of 91 - 94° at 85 mm: 513(2), 538(3), 578(3), 618(2), 658(4), 693(2), 737(4), 1187(3), 1351(2), 1380(3), 1444(5), 1640(3), 1668(8), 2872(4), 3013(2), 3078(2).

A comparison of the intensity of the three-membered ring frequencies with those of the double bonds indicated a substantial predominance of the unsaturated chlorides.

Splitting hydrogen chloride out of Fractions 2 and 3. 15 g of the chloride were added to a solution of 25 g of KOH in 70 g of ethyl cellosolve heated to boiling. The experimental conditions employed were those described above for the synthesis of cyclopropylacetylene. The yield of the hydrocarbon was 2.7 g, or 88% of the theoretical. The hydrocarbon had a b.p. of 54 - 57° (776mm) after desiccation with calcium chloride. The hydrocarbon exhibited positive reactions with Behal's reagent and with ammoniacal cuprous chloride. It colored tetranitromethane a bright yellow.

d_4^{20} 0.7584; n_D^{20} 1.44742; MR_D 23.27. C_5H_6 F F. Calculated MR_D 22.76. Exaltation: 0.51.

Raman spectrum of the hydrocarbon: 145(4), 172(3), 207(4), 259(2), 319(3), 361(2), 399(2), 463(2), 488(2), 518(2), 587(1), 612(1), 648(1), 683(1), 718(1), 752(2), 791(1), 820(2broad), 860(1), 875(1), 938(3), 1001(2), 1033(2), 1082(2), 1111(2), 1163(4), 1187(3), 1288(5), 1351(6), 1378(3), 1412(5), 1454(1), 1478(1), 1586(2), 1609(8), 2098(4), 2122(3), 2189(2), 2237(10), 2839(2), 2860(2), 2889(2), 2921(4), 3013(3), 3023(3), 3087(3) (the frequencies underlined refer to cyclopropylacetylene.)

SUMMARY

1. Cyclopropylacetylene has been synthesized, and its constants and Raman spectrum given.

2. It has been shown that "vinyltrimethylene bromide" is not an individual substance, but contains an open-chain isomeric dibromide.

3. The reaction of acetylcyclopropane with PCl_5 has been investigated.

4. It has been shown that the presence of two chlorine atoms at the α-position to the three-membered ring promotes the latter's cleavage.

5. Splitting hydrogen chloride out of the mixture of dichlorides produced by reacting acetylcyclopropane with PCl_5 yields a hydrocarbon mixture that contains constituents with conjugated acetylene-ethylene bonds, in addition to cyclopropylacetylene.

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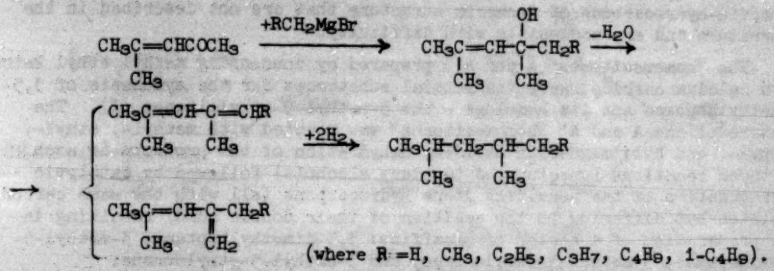
SYNTHESIS OF HYDROCARBONS

VII. HOMOMESITONES IN THE SYNTHESIS OF PARAFFIN HYDROCARBONS OF ISOMERIC STRUCTURE

R.Ya.Levina, N.P.Shusherina, E.G.Treshchova, and V.M.Tatevsky

In one of our previous reports [1] we described the synthesis of 2,4-dimethylalkanes, involving the following series of reactions:

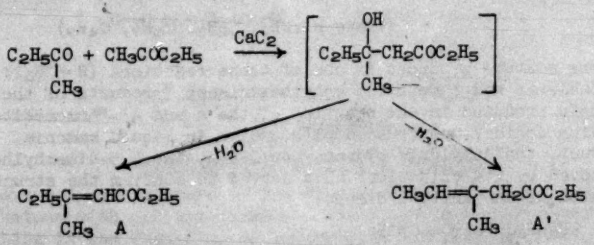


(where R = H, CH_3, C_2H_5, C_3H_7, C_4H_9, 1-C_4H_9).

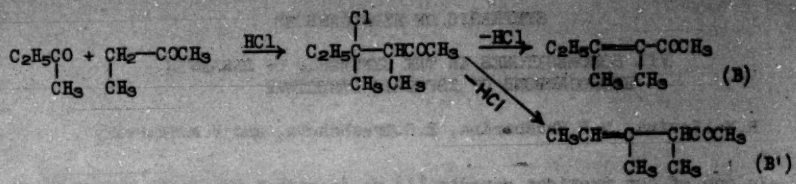
The initial substance for these syntheses was the readily available unsaturated ketone mesityl oxide. We were interested in employing homologs of mesityl oxide, the so-called "homomesitones," as initial substances in similar reactions to synthesize alkanes of isomeric structure.

The structure of the "homomesitones" - unsaturated ketones produced by condensing methyl ethyl ketone with various condensing agents, both alkaline and acid - has been often discussed in the literature.

It has been established that alkaline agents condense methyl ethyl ketone at the expense of the hydrogen atoms in the methyl group, yielding 3-methylhepten-3-one-5 ("homomesitone" A [2,3]) with some of another ketone A' that has the same carbon skeleton but has the double bond in another position - 3-methylhepten-2-one-5 [3].

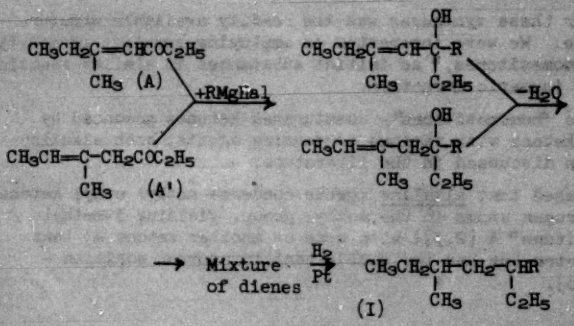


The condensation of methyl ethyl ketone by acid agents involves the hydrogen atoms of the methylene group, yielding a mixture of two unsaturated ketones (3,4-dimethylhexen-3-one-5 (B) and 3,4-dimethylhexen-2-one-5 (B') [2,3], again differing solely in the position of the double bond:



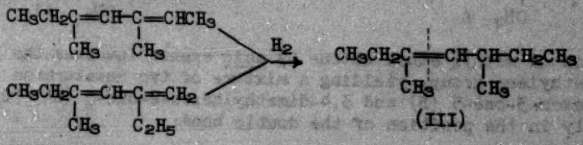
In the present research we utilized "homomesitones" to synthesize some paraffin hydrocarbons of isomeric structure that are not described in the literature and are accessible with difficulty.

The "homomesitones" A and A', prepared by condensing methyl ethyl ketone with calcium carbide, were the initial substances for the synthesis of 3,5-dimethylheptane and its homologs - the 3-methyl-5-ethylalkanes (I). The mixture of the A and A' "homomesitones" was reacted with methyl-, ethyl-, propyl-, and butylmagnesium halides, dehydration of the products of each of these reactions (unsaturated tertiary alcohols) followed by catalytic hydrogenation of the resulting diene hydrocarbons (all with the same carbon skeleton but differing in the position of their double bond) resulting in the preparation of a series of paraffins: 3,5-dimethylheptane, 3-methyl-5-ethylheptane, 3-methyl-5-ethyloctane, and 3-methyl-5-ethylnonane:



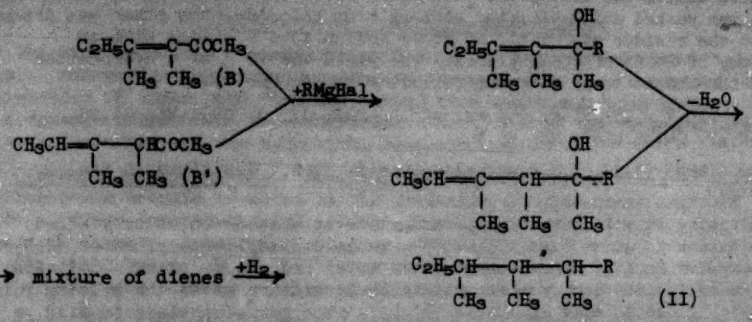
(where R = CH_3, C_2H_5, C_3H_7, C_4H_9)

The diene mixture produced in one of these reactions (R = CH_3): 3,5-dimethylheptadienes and 3-methyl-5-ethylhexadienes (products of the dehyration of the alcohols produced in the reaction of the A and A' "homomesitones" with methylmagnesium iodide) was reduced with sodium in liquid ammonia. The reduction product, the ethylenic hydrocarbon C_9H_{18}, was 3,5-dimethylheptene-3 (III), as proved by its oxidation; this served to confirm the structure of the carbon skeleton of the initial dienes:



The mixture of the B and B' "homomesitones," produced by condensing methyl ethyl ketone with hydrogen chloride, and reacting the resulting β-chloroketone with pyridine, served as the initial substances for the synthesis of paraffin hydrocarbons of different structure (II): 2,3,4-trimethylhexane and its homologs - 3,4,5-trimethylheptane.

The mixture of the B and B' "homomesitones" was reacted with methylmagnesium iodine and ethylmagnesium bromide; dehydration of the unsaturated tertiary alcohols produced in each instance resulted in the formation of mixtures of diene hydrocarbons (having the same carbon skeleton in each instance,) which yielded 2,3,4-trimethylhexane and 3,4,5-trimethylheptane upon catalytic hydrogenation.



(where R = CH_3 and C_2H_5)

The structure of the synthesized hydrocarbons of both series (I and II), stemming from the very method of synthesis, was confirmed by comparing the Raman spectra of two isononanes (representatives of each of these series: 3,5-dimethylheptane and 2,3,4-trimethylhexane), with the spectra given in the literature for these hydrocarbons.

Hence, the reaction of the "homomesitones" (unsaturated ketones produced by the condensation of methyl ethyl ketone by alkaline and acid agents) with organomagnesium compounds may be utilized as a method of synthesizing alkanes of a definite structure: 3,5-dimethylheptane and 2,3,4-trimethylhexane, as well as their homologs: 3-methyl-5-ethylalkanes (I) and 3,4,5-trimethylalkanes (II):

(I) (II)

EXPERIMENTAL

Synthesis of 3,5-Dimethylheptane

The preparation of a mixture of the "homomesitones" A and A' (by condensing methyl ethyl ketone with calcium carbide), their reaction with methylmagnesium iodide, resulting in the formation of unsaturated tertiary alcohols, and the preparation of dienes from them by means of dehydration have been described in detail in one of our preceding reports [4].

The resulting mixture of dienes (3,5-dimethylheptadienes and 3-methyl-5-ethylhexadienes) with a yield of 86%, based on the "homomesitones," [1] had the

1) The yield of 86% of the theoretical was secured with the following proportions of the homomesitone, methyl iodide, and magnesium: 1:1.5:1.5. The yield of dienes dropped to 40% of the theoretical when equimolecular quantities of these components were used.

following constants after distillation above sodium into a tower:

B.p. 136 - 142° at 760 mm; n_D^{20} 1.4495; d_4^{20} 0.7675; MR_D 43.40
$C_9H_{16}F_2$. Calculated: MR_D 42.82; EM_D 0.62.

Partial reduction of the mixture of 3,5-dimethylheptadienes and 3-methyl-5-ethylhexadienes with sodium in liquid ammonia. An ether solution of 17 g of the alkadiene mixture (136-142°) was added, with constant stirring, to a solution of 25 g of sodium in liquid ammonia (-50 to -60°), after which stirring was continued for another 5 - 6 hours at the same chilling temperature. Then 100 ml of absolute ether were added, and the reaction mass was allowed to stand overnight at room temperature to evaporate the ammonia. The next day the excess sodium was decomposed with water under the ether layer. The ether extract was washed and desiccated with calcium chloride, the ether was driven off, and the residue was distilled above sodium into a column with an efficiency of 25 theoretical plates. The yield was 12 g of a hydrocarbon (70% of the theoretical) with the following constants:

B.p. 130.7 - 131.2° at 755 mm; n_D^{20} 1.4222; d_4^{20} 0.7399; MR_D 43.55.
$C_9H_{18}F$. Calculated: MR_D 43.30.

The alkene (III), 3,5-dimethylheptene-3, is not described in the literature.

Oxidizing it with potassium permanganate in acetone solution yielded methylethylacetic acid, b.p. 173 - 175°, whose p-phenylphenacyl ester ($C_2H_5CH(CH_3)COOCH_2COC_6H_4C_6H_5$), was prepared; the ester had a m.p. of 65 - 66° after triple recrystallization from alcohol. The literature gives the melting point of methylethylacetic acid as 175 - 176° [5]. The methylethylacetic acid we synthesized by utilizing sodium malonic ester had a m.p. of 174 - 176°, while the m.p. of its phenylphenacyl ester was 66°; the mixed melting point of the latter ester with the p-phenylphenacyl ester of the acid produced by oxidizing the alkene was the same: 66°.

Hence, the oxidation products of the alkene produced by partially reducing the alkadiene mixture turned out to be methylethylacetic acid, which proved that the structure of the alkene was that of 3,5-dimethylheptene-3, thus confirming the structure of the carbon skeleton in the original alkadienes.

Catalytic hydrogenation of the mixture of 3,5-dimethylheptadienes and 3-methyl-5-ethylhexadienes - synthesis of 3,5-dimethylheptane. The mixture of dienes with a b.p. of 136 - 142° was passed over platinized charcoal at 165° in a current of hydrogen. The resulting 3,5-dimethylheptane was distilled above sodium (into a column with an efficiency of 25 theoretical plates). Its constants and analysis are given in Tables 3 and 4. A Raman spectrum was taken of the synthesized alkane.

The spectrum was made with a Steinheil spectrograph, using the customary slit width of 6 cm^{-1}, the intensity of the lines was measured visually on a nominal scale on which the intensity of the 1450 cm^{-1} frequency was taken as 10 units.

In comparing our spectrum (comprising 30 lines) with the spectrum of 3,5-dimethylheptane secured by Fenske [6] (Table 1), we found that several frequencies in our spectrum were absent in Fenske's spectrum.

Inasmuch as the hydrocarbon spectra recorded by that author were made with a spectrograph having a slit width of 15 cm^{-1}, we re-recorded the 3,5-dimethylheptane spectrum with a 15 cm^{-1} slit. The new spectrum we secured

consisted of 26 lines. Some of the lines that were resolved in the spectrum photographed with a slit width of 6 cm^{-1} formed wide bands that ran together into a single line in the spectrum made with the 15 cm^{-1} slit.

The spectrum we photographed with the 15 cm^{-1} slit coincided in general with Fenske's spectrum, but had two more lines; apparently the photoelectric method that Fenske used did not enable him to record lines of low intensity. To confirm this conclusion we compared the finding obtained by P.A.Bazhulin, B.A.Kazansky, and their associates [7], using a 6 cm^{-1} slit with those obtained by Fenske [6] with a 15 cm^{-1} slit for the spectra of several branched hydrocarbons. We found that there was the same difference between the spectra recorded by these authors for numerous hydrocarbons.

Synthesis of 3-Methyl-5-Ethylalkanes

The mixture of the "homomesitones" A and A' was reacted with ethyl-, propyl-, and butyl- magnesium bromides by the method we have described [4] for the reaction of these same "homomesitones" with methylmagnesium iodide, though the component proportions were different - 1:1.2:1.2 of the "homomesitone," the alkyl bromide, and the magnesium, respectively.

3-Methyl-5-ethylheptane. Reacting the "homomesitones" A and A' with ethylmagnesium bromide resulted in the formation of unsaturated tertiary alcohols, which were then dehydrated by distillation with iodine. The resultant mixture of dienes - 3-methyl-5-ethylheptadiene-3,5 and 3-methyl-5-ethylheptadiene-2,4 (the yield being 52% of the theoretical, based on the intial "homomesitones") had the following constants after distillation above sodium into a column:

B.p. 156 - 160° at 751 mm; n_D^{20} 1.4510; d_4^{20} 0.7740; MR_D 48.08. $C_{10}H_{18}F_2$. Calculated: MR_D 47.45; EM_D 0.63.

TABLE 1

Raman Spectrum of 3,5-Dimethylheptane

3,5-Dimethylheptane, produced by hydrogenating a mixture of alkadienes (136-142°) (slit width 6 cm^{-1}).	320(3), 367(0.5), 413(0.5), 449(2,r), 467(0.5), 766(3.5), 792(1,r), 822(2.5), 833(2), 864(0.5), 894(1.5), 935(1.5,r), 963(0), 985(3,h), 996(1), 1038(1.5), 1055(2), 1085(0.8), 1149 (2,h), 1170(2.5), 1189(0), 1227(0.5), 1269(2.5), 1298 (1), 1325(0.5), 1355(3), 1382(0), 1440 (10 s), 1460(9,h).
3,5-Dimethylheptane, according to Fenske (slit width 15 cm^{-1})	318(0.020), 447(0.032), 767 (0.045), 824(0.055), 892(0.019), 936(0.019), 987(0.060), 1039 (0.044), 1160(0.053), 1283(0.023), 1304(0.014), 1356(0.035), 1456(0.179).

Hydrogenation of the resultant diene mixture at 170° above platinized charcoal yielded the paraffin hydrocarbon 3-methyl-5-ethylheptane, which was distilled above sodium into a column with an efficiency of 40 theoretical plates. The constants and analysis of the synthesized 3-methyl-5-ethylheptane are listed in Tables 3 and 4.

3-Methyl-5-ethyloctane. Reacting a mixture of the "homomesitones" A and A' with propylmagnesium bromide yielded unsaturated tertiary alcohols, dehydration of which (by distillation with iodine) yielded a mixture of dienes, 3-methyl-5-ethyloctadienes and 3-methyl-5-propylheptadienes, which had the same carbon skeleton (the yield was 66% of the theoretical, based on the "homomesitones"). The alkadiene mixture had the following constants after distillation above

sodium into a column:

B.p. 173 - 175° at 759 mm; n_D^{20} 1.4350; d_4^{20} 0.7784; MR_D 52.85. $C_{11}H_{20}F_2$. Calculated: MR_D 52.06; EM_D 0.79.

Catalytic hydrogenation of this alkadiene mixture yielded 3-methyl-5-ethyloctane, which was distilled above sodium into a column with an efficiency of 40 theoretical plates. Its constants and analysis are listed in Tables 3 and 4.

3-Methyl-5-ethylnonane. Reaction of the mixture of the "homomesitones" A and A' with butylmagnesium bromide yielded unsaturated tertiary alcohols, dehydration of which (by distillation with iodine) yielded a mixture of dienes, 3-methyl-5-ethylnonadienes and 3-methyl-5-butylheptadienes, which had the same carbon skeleton (the yield was 50% of the theoretical based on the "homomesitones"). The alkadiene mixture had the following constants after distillation above sodium into a column:

B.p. 188 - 191° at 750 mm; n_D^{20} 1.4525; d_4^{20} 0.7874; MR_D 57.01. $C_{12}H_{22}F_2$. Calculated: MR_D 56.68; EM_D 0.33.

Catalytic hydrogenation of this alkadiene mixture at 170° above platinized charcoal yielded 3-methyl-5-ethylnonane, which was distilled above sodium into a column with an efficiency of 40 theoretical plates. Its constants and analysis are listed in Tables 3 and 4.

Synthesis of 2,3,4-Trimethylhexane and 3,4,5-Trimethylheptane

Preparation of a mixture of the "homomesitones" B and B' (3,4-dimethylhexen-3-one-5 and 3,4-dimethylhexen-2-one-5.) Methyl ethyl ketone (430 g) was saturated with anhydrous hydrogen chloride (140 g) at room temperature, the resultant mixture being allowed to stand for 48 hours and then treated with 400 ml of water. The layer of 3-chloro-3,4-dimethylhexanone-5 was separated, desiccated with calcium chloride, and distilled in vacuo (b.p. 124 - 126° at 150 mm; yield 200 g). The synthesized β-chloroketone was boiled with pyridine (100 g) for four hours to split off hydrogen chloride. After the reaction mixture had cooled, the reaction product was filtered to remove the crystalline precipitate of pyridine hydrochloride, washed repeatedly with a 20% aqueous solution of alkali and with water, desiccated with calcium chloride, and distilled two or three times to eliminate its dissolved pyridine hydrochloride. Subsequent fractional distillation (into a column) yielded a mixture of the "homomesitones" B and B' (95 g, or 61% of the theoretical, based on the 3-chloro-3,4-dimethylhexanone-5 used), which had the following constants:

B.p. 156.5 - 160° at 760 mm; n_D^{20} 1.4410; d_4^{20} 0.8660. The literature [3] gives the following constants for the "homomesitones" B and B': for 3,4-dimethylhexen-3-one-5 (B) - b.p. 160° at 750 mm; n_D^{18} 1.4529; d_4^{17} 0.8685. and for 3,4-dimethylhexen-2-one-5 (B') - b.p. 154° at 750 mm; n_D^{20} 1.4377; d_4^{20} 0.8539.

The mixture of the "homomesitones" B and B' was reacted with organomagnesium compounds (proportions of the components: the ketone, the alkyl halide, and the magnesium, were 1:1.5:1.5, respectively) under the conditions set forth in our preceding report [4] for the reaction of methylmagnesium iodide with the "homomesitone" A.

2,3,4-Trimethylhexane. The reaction of the mixture of the "homomesitones" B and B' with methylmagnesium iodide yielded unsaturated tertiary alcohols, dehydration of which (by distillation with iodine) produced a mixture of dienes, 2,3,4-trimethylhexadienes, the yield being 65% of the theoretical, based on the initial mixture of unsaturated ketones. After it had been distilled above sodium (into a column), the resulting mixture of 2,3,4-trimethylhexadienes had the

following constants:

B.p. 130.7 - 133.5° at 748 mm; n_D^{20} 1.4451; d^{20} 0.7649; MR_D 43.22. $C_9H_{18}F_2$. Calculated: MR_D 42.82; EM_D 0.4.

Figures in the literature [8] for 2,3,4-trimethylhexadienes: b.p. 134 - 135° at 768 mm; n_D^{20} 1.4425; d_4^{20} 0.7701.

Catalytic hydrogenation of the mixture of 2,3,4-trimethylhexadienes at 170° above platinized charcoal yielded the isononane, which could also be assigned the structure of 2,3,4-trimethylhexane. The resultant alkane was distilled above sodium into a column with an efficiency of 50 theoretical plates (its constants and analysis are listed in Tables 3 and 4).

The structure of the synthesized isononane was confirmed by analysis of its Raman spectrum.

The spectrum was recorded under the conditions described above. All the principal spectral lines coincided with the strong lines of the 2,3,4-trimethylhexane spectrum cited by Fenske [6] (Table 2). Our spectrum proved to be much richer in lines, and in it lines were resolved that ran together into a single band in Fenske's spectrum. This discrepancy may be attributed to the differences in the recording conditions cited above, as well as to the lower sensitivity of the photoelectric method employed by Fenske.

TABLE 2

Raman Spectrum of 2,3,4-Trimethylhexane

2,3,4-Trimethylhexane synthesized in the present research	274 (0.2, r; h), 333 (2.5, r), 357 (0.1), 397-401 (0.4, r), 434 (1), 466 (4, r), 471 (1), 516 (0.3), 570 (1), 586 (1), 676 (0), 735 (1.5), 746 (2.5, h), 764 (1.5), 769 (1.5), 779 (1.5), 806 (1.5), 822 (1.8, h), 875 (3.5), 896 (0.3), 915 (3.5), 956 (4), 978 (1), 996 (1.8), 1031 (2), 1056 (1), 1085 (0.8), 1107 (0.5, r; h), 1165 (4), 1183 (1.5), 1258 (0.1, h), 1270 (0.3), 1292 (2), 1315 (0.5), 1323-1327 (1.5 ... 0.8), 1355 (2), 1382 (1), 1448 (10, h), 1463 (10), 2809 (2.5), 2864, (2.5), 2877 (6, h), 2916 (3.5), 2943 (3.5), 2968 (4, r), 3032 (2).
2,3,4-Trimethylhexane, according to Fenske	325 (0.025), 404 (0.016), 462 (0.057), 596 (0.016), 754 (0.069), 812 (0.037), 874 (0.038), 918 (0.032), 957 (0.044), 1000 (0.030), 1029 (0.024), 1166 (0.068), 1292 (0.023), 1330 (0.030), 1460 (0.177).

3,4,5-Trimethylheptane. Reacting a mixture of the "homomesitones" B and B' with ethylmagnesium bromide yielded a mixture of unsaturated tertiary alcohols. Dehydrating this latter mixture by passing it over chromic oxide on alumina at 250° in a current of nitrogen resulted in the formation of a mixture of dienes, 3,4,5-trimethylheptadienes and 3,4-dimethyl-5-ethylhexadienes, which had the same carbon skeleton, the yield being 65% of the theoretical, based on the initial mixture of "homomesitones". The alkadiene mixture had the following constants after distillation above sodium (into a column):

B.p. 155-160° at 765 mm; n_D^{20} 1.4520; d_4^{20} 0.7797; MR_D 47.83. $C_{10}H_{18}F_2$. Calculated: MR_D 47.45; EM_D 0.38.

According to the literature [8], a mixture of dienes produced in the same manner distilled at 149-159° at 743 mm.

TABLE 3

Structure of hydrocarbon	R	Name of hydrocarbon	Melting point	n_D^{20}	n_4^{20}	MR_D Expt.	MR_D Calc.
C-C-C-C-C-R | | C C-C (I)	CH_3	3,5-Dimethylheptane[1].....	134.6-135° (760 mm)	1.4070	0.7199	43.86	43.76
	C_2H_5	3-Methyl-5-ethylheptane....	158.2-158.4 (762 mm)	1.4164	0.7406	48.25	48.38
	C_3H_7	3-Methyl-5-ethyloctane.....	176-176.5 (765 mm)	1.4204	0.7486	52.88	52.99
	C_4H_9	3-Methyl-5-ethylnonane.....	195-195.2 (768 mm)	1.4260	0.7583	57.55	57.61
C-C-C-C-C-R | | | C-C-C	CH_3	2,3,4-Trimethylhexane[1].....	137.6-137.8 (770 mm)	1.4138	0.7347	43.93	43.76
	C_2H_5	3,4,5-Trimethylheptane.....	161.8-162.4 (766 mm)	1.4212	0.7515	48.06	48.38

TABLE 4

Hydrocarbon	Mg of subst.	Mg CO_2	Mg H_2O	% Found C	% Found H	% Calculated C	% Calculated H	General formula
3,5-Dimethylheptane...	4.440	13.770	6.130	84.58	15.45	84.38	15.62	C_9H_{20}
	5.010	15.530	6.850	84.54	15.33			
3-Methyl-5-ethylheptane.....	4.235	13.100	5.920	84.42	15.64	84.41	15.59	$C_{10}H_{22}$
	3.647	11.280	5.110	84.38	15.68			
3-Methyl-5-ethyloctane	7.200	22.300	9.920	84.52	15.42	84.70	15.30	$C_{11}H_{24}$
	4.010	12.410	5.530	84.46	15.43			
3-Methyl-5-ethylnonane	4.540	14.230	6.275	84.36	15.47	84.63	15.37	$C_{12}H_{26}$
	4.365	13.500	6.070	84.40	15.56			
2,3,4-Trimethylhexane	5.300	16.360	7.390	84.24	15.60	84.38	15.62	C_9H_{20}
	5.900	18.245	8.215	84.38	15.58			
3, 4,5-Trimethylheptane.....	4.210	13.000	5.870	84.27	15.60	84.41	15.59	$C_{10}H_{22}$
	5.265	16.270	7.530	84.33	15.62			

Catalytic hydrogenation of the resultant mixture of dienes (155-160°) at 170° above platinized charcoal yielded 3,4,5-trimethylheptane, which was distilled above sodium into a column with an efficiency of 50 theoretical plates. Its constants and analysis are listed in Tables 3 and 4.

[1]) Fenske [6] cites the following constants for 3,5-dimethylheptane and 2,3,4-trimethylhexane without indicating the method of synthesis employed: b.p. 136° at 760 mm; n_D^{20} 1.4067; and b.p. 139.1° at 760 mm; n_D^{20} 1.4144, respectively.

SUMMARY

1. A method has been developed for synthesizing the difficultly accessible isomeric paraffin hydrocarbons 3,5-dimethylheptane and its homologs: the 3-methyl-5-ethylalkane. The method involves a reaction between a mixture of the "homomesitones" 3-methylhepten-3-one-5 and 3-methylhepten-2-one-5 (products of the condensation of methyl ethyl ketone with calcium carbide) and organomagnesium compounds, followed by dehydration of the products of this reaction – unsaturated tertiary alcohols – and catalytic hydrogenation of the resultant dienes.

We have thus synthesized 3,5-dimethylheptane, 3-methyl-5-ethylheptane, 3-methyl-5-ethyloctane, and 3-methyl-5-ethylnonane, not hitherto described in the literature.

2. A method has been developed for synthesizing the difficultly accessible isomeric paraffin hydrocarbons: 2,3,4-trimethylhexane and its homologs, the 3,4,5-trimethylalkanes. The method involves a reaction between a mixture of the "homomesitones" 3,4-dimethylhexen-3-one-5 and 3,4-dimethylhexen-2-one-5 (condensation products of methyl ethyl ketone with hydrogen chloride) and organomagnesium compounds, followed by dehydration of the products of this reaction – unsaturated tertiary alcohols – and catalytic hydrogenation of the resultant dienes.

We have thus synthesized 2,3,4-trimethylhexane and 3,4,5-trimethylheptane, not hitherto described in the literature.

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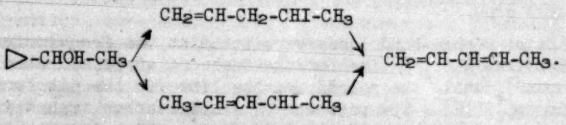
THE ACTION OF PCl_3 AND PBr_3 UPON METHYLCYCLOPROPYLCARBINOL

Ya. M. Slobodin and I. N. Shokhor

In our preceding report we cited our data on the synthesis of methylcyclopropylcarbinol [1]. In view of the fact that the halogen derivatives obtainable from this carbinol have not been described adequately [2, 3], we were interested in learning the conditions required for their formation as well as their stability.

N. Ya. Demyanov long ago [4] demonstrated that iodine and phosphorus react with methylcyclopropylcarbinol to produce quantitative polymerization, the three-membered ring being ruptured and an unsaturated iodide being formed.

Splitting hydrogen iodide out of the latter yields piperylene:



Although the author was unable to prove the structure of the iodide by oxidizing it and analyzing the resultant products, he adopted the structures cited above as the most probable ones.

In our present research we reacted methylcyclopropylcarbinol with PBr_3 in the presence of pyridine [2], securing a mixture of bromides, which was found to contain two isomeric monobromides upon chemical and spectroscopic analysis. One of these monobromides was the normal reaction product, containing the cyclopropane ring (I), while the other contained a double bond (II):

▷-CHBr-CH_3 (I) $CH_2Br-CH_2-CH=CH-CH_3$. (II)

The Raman spectrum exhibited the double-bond frequency 1668 cm^{-1}, which identified the unsaturated bromide as a disubstituted ethylene. The spectrum was also found to contain intensive C-Br bond lines, with frequencies of 568, 638, and 598 cm^{-1}, indicating that the $-CH_2Br$ and $=CHBr$ groups were present [6].

The presence of the cyclopropane ring was confirmed by the presence of the 747, 826, 899, 1026, 1192, 1492, 3016, and 3067 cm^{-1} frequencies in the spectrum.

The formation of 5-bromopentene-2 is due to the isomerization of the cyclic bromide

▷-CHBr-CH_3 → $CH_2Br-CH_2-CH=CH-CH_3$.

To prove that the $-CH_2Br$ group was present in the unsaturated bromide, the latter was converted into an ester by the action of silver acetate. The ester was hydrogenated with a platinum catalyst and then saponified with an aqueous solution of potash. The resultant alcohol was converted into an aldehyde by passing it over a catalyst (zinc sulfide on pumice). The resultant aldehyde was identified by means of its derivative with 2,4-dinitrophenylhydrazine (m.p. 98°), which is normal valeraldehyde.

Splitting the hydrohalide out of 5-bromopentene may result in formation of nothing but piperylene, which Demyanov secured from the iodide long ago. It may be conjectured the structure of the iodide corresponded to the structure we have cited for the unsaturated bromide, since the oxidation products recovered by Demyanov contained neither β-iodobutyric nor α-iodopropionic acid [4].

The ratio of the unsaturated bromide to the trimethylenic bromide was 2:1.

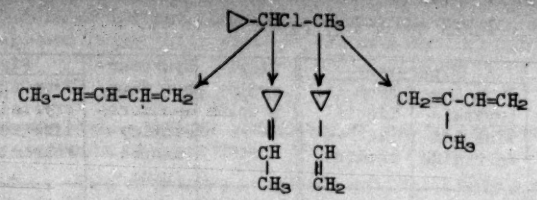
The reaction of PCl_3 with methylcyclopropylcarbinol is different. The principal reaction product is the normal one – α-chloroethylcyclopropane (80%). The impurities were a slight quantity of a hydrocarbon and an unsaturated chloride.

The Raman spectra exhibited the strong frequency of 1191 cm^{-1} for a three-membered ring, as well as the frequencies of 762, 821, 1029, 1430, 3013, and 3083 cm^{-1} for the same ring.

Two very faint double-bond lines were found at the frequencies of 1640 and 1659 cm^{-1}. The first was the line for the trace of an unsaturated hydrocarbon (vinylcyclopropane), while the second was the line for the cis form of chloropentene-2 (1658 cm^{-1}) [7]. The presence of a hydrocarbon impurity in the chloride was likewise borne out by the analytical findings, which invariably exhibited too low a percentage of chlorine. The percentage of both products in the chloride could be estimated as no more than 10% of each from the intensities of the double-bond frequencies.

The data set forth below enable us to assert that these impurities are vinylcyclopropane and 5-chloropentene-2, as already stated. When hydrogen chloride was split out of α-chloroethylcyclopropane, we might have expected that the formation of vinylcyclopropane would be paralleled by the formation of ethylidenecyclopropane, which has never been synthesized hitherto and the very existence of which has been doubted, since there are no dependable reports that anyone has ever been able to secure derivatives of cyclopropane containing a heptacyclic double bond [8-16]. We ran direct tests on splitting hydrogen chloride out of α-chloroethylcyclopropane. They yielded a hydrocarbon mixture with a b.p. of 40.5-42.5° (755 mm), whose Raman spectrum disclosed two very intensive double-bond frequencies, 1640 and 1655 cm^{-1}. The first of these frequencies is that of the double bond of the hydrocarbon impurity in the chloride. Thorough study of the Raman spectrum of the hydrocarbon mixture indicated that it contained all the frequencies characteristic of the three-membered ring. Comparison of the vinylcyclopropane spectrum with the one we photographed for a hydrocarbon prepared by the Demyanov and Doyarenko method [4] enabled us to provide a definite answer to the question of whether vinylcyclopropane was present in the hydrocarbon mixture (secured when hydrogen chloride was split out of α-chloroethylcyclopropane) as one of the mixture's constituents. The spectroscopic findings indicated that an unsaturated hydrocarbon was another constituent of this mixture. Its double-bond frequency (1655 cm^{-1}) is quite different from the frequency of the vinylcyclopropane double bond (1640 cm^{-1}).

The splitting of elements of hydrogen chloride out of the chloride may result in the formation of the following four hydrocarbons:



No lines were found in the Raman spectrum of the hydrocarbon mixture whose frequencies might have given any indication of the presence of isoprene. On the other hand, the presence of all the characteristic frequencies of piperylene, with the sole exception of the double-bond frequency (1646 cm^{-1}, according to the literature), indicates that this compound is present. To clear up the discrepancy between the data in the literature and the data we had secured for the hydrocarbon mixture, we photographed the spectra of the piperylene prepared from its crystalline tetrabromide with a m.p. of 113-114°, the piperylene prepared from its liquid tetrabromide, and the piperylene prepared by rectifying the technical product. As we see from the appended table, piperylene, in contrast to the data in the literature, contains four frequencies identifying its conjugated system. Two of them are strong frequencies, 1646 and 1655 cm^{-1}, the other two (1596 and 1603 cm^{-1}) being weak. It must be assumed that these frequencies refer, in pairs, to the cis and trans forms of piperylene. The table does not include the Raman spectrum of the piperylene produced by rectifying the technical product, as its sole difference lies in the different intensity of the double-bond frequencies, and hence, merely a different ratio between the cis and trans forms.

The spectrum of the hydrocarbon produced by splitting hydrogen chloride out of the α-chloroethylcyclopropane contains the 1603 and 1655 cm^{-1} frequencies, the 1646 cm^{-1} frequency being absent. This indicates that only trans-piperylene is formed when the cylopropane ring is opened.

The piperylene is formed in two stages. The first stage is the result of the isomeric conversion of the α-chloroethylcyclopropane, while the second is the result of the splitting out of the hydrogen chloride.

Hence, of the four possible dehalogenation products, we have found vinylcyclopropane and piperylene. It is hardly likely that isoprene is formed, for this would involve the rupture of the three-membered ring at an unsubstituted carbon atom, which is contradicted by the findings of many authors. We found no ethylidenecyclopropane, but this does not entitle us to assert that it cannot exist.

The hydrocarbon added 23% more hydrogen than would have been required for a single double bond, when it was hydrogenated quantitatively above a platinum catalyst.

When the hydrocarbon mixture was brominated, we secured a crystalline tetrabromide with a m.p. of 114.5°, whose mixed melting point with piperylene tetrabromide or with vinyltrimethylene dibromide exhibited no depression.

The following aldehydes were found after ozonolysis of the hydrocarbon mixture: formaldehyde, acetaldehyde, and cyclopropylformaldehyde.

It follows from what has been set forth above that the nature of the halogen atom at the alpha position to the trimethylene ring has a great influence upon the ring's stability. Whereas the bromine atom produces complete cleavage of the ring (Demyanov), the bromine atom effects only partial ring cleavage, and the chlorine

Raman Spectra (Frequencies in cm^{-1})

Vinylcyclopropane	Hydrocarbon from α-chloroethylcyclopropane	Piperylene		Vinylcyclopropane	Hydrocarbon from α-chloroethylcyclopropane	Piperylene	
		From the crystalline tetrabromide	From the liquid tetrabromide			From the crystalline tetrabromide	From the liquid tetrabromide
	386(3)	386(5)	386(5)	1321(2)	1324(1)		1324(1)
448(6 broad)	448(5 broad)			1374(2)	1379(2)	1376(6)	1376(5)
	478(4)	478(5)	478(5)	1416(2)	1413(2)	1413(5)	1413(4)
762(4)	764(3)			1428(8)	1430(5)	1432(3)	1434(2)
816(8)	816(5)	814(1)	816(1)	1452(6)	1451(5)	1451(6)	1451(6)
884(5 broad)	889(4 broad)			1582(1)	1586(1)	1596(4)	
896(5 broad)	898(4 broad)	897(4)	897(3)		1603(1)	1603(4)	1602(6)
938(10)	938(6)			1640(10)	1640(8)	1646(10)	1646(2)
991(2 broad)	994(1)	955(1)	955(1)		1655(10)	1655(10)	1455(10)
1020(5)	1020(2)	1032(1)	1034(1)		2877(4 broad)	2860(3)	2877(3)
1129(2)	1076(1)					2887(2)	
	1174(3)	1174(3)	1172(3)		2921(4 broad)	2921(6)	2919(5)
1186(10)	1186(10)	1183(7)	1184(6)				2960(2)
1201(1)						2996(5)	2998(5)
1239(3 broad)	1239(2)			3005(5 broad)	3005(5 broad)		
	1248(2 broad)	1250(8)	1248(6)	3082(5 broad)	3082(5)	3083(2)	3087(2)
1292(8)	1292(8)	1292(10)	1290(10)				

atom produces only slight ring cleavage. Hence, the action of PCl_3 upon the cyclopropane carbinols is of practical usefulness in synthesizing derivatives of this series.

EXPERIMENTAL

α-Bromoethylcyclopropane. 5 grams of anhydrous pyridine were added to 10 g of methylcyclopropylcarbinol with a b.p. of 121.5-123°, dissolved in 50 ml of anhydrous ether [5]. Then 15 g of PBr_3 were slowly added to the mixture from a dropping funnel. The influx rate was regulated so as to keep the temperature of the mixture from exceeding 30-35°. After all the PBr_3 had been added, another 3 g of pyridine were poured into the mixture, and the mass was allowed to stand at room temperature for an hour. Then the mixture was poured out into ice water. The ether layer was separated, and the aqueous layer extracted with ether. The combined ether extracts were desiccated with calcium chloride. After the ether had been driven off, a yellowish oil with an acrid odor was left within the flask. Nearly all the bromide boiled off at 58-61° and 40-45 mm. Only a negligible residue was left within the distilling flask. Refractionation at 752 mm yielded the following fractions: 1) 121-123°, 2 g; 2) 123-124°, 7 g; and 3) 124-126°, 0.5 g.

Slight evolution of HBr was observed during fractionation, and a hydrocarbon odor was perceived. The total yield of the bromide (121-126°) was 55% of the theoretical.

d_4^{20} 1.2651; n_D^{20} 1.46811; MR_D 32.74; Calc. 30.85.

The excessively high molecular refraction is due to the presence of unsaturated open-chain compounds as impurities.

0.2122 g subs.; 0.2620 g AgBr; 0.3959 g subs.: 0.4889 g AgBr.
Found %: Br 52.74, 52.60. C_5H_9Br. Calculated %: Br 53.69.

Determination of the bromine number in the monobromide indicated that its unsaturation was 67%. It should be noted that this method is unreliable for mixtures that contain cyclopropane compounds. The unsaturation is found to be too high when the compound is kept in contact with the bromine solution for a long time, even in the dark. It goes as high as 78%, and even 87%, depending upon the time of contact.

Raman spectrum: 145(2), 168(2), 221(3), 263(2), 292(2), 315(8), 391(1), 458(1), 482(1), 568(6 broad), 598(6 broad), 638(10 broad), 683(3), 747(2), 784(1), 826(1), 899(6), 965(1), 987(1), 1026(1), 1079(1), 1105(1), 1149(1), 1192(4), 1219(2), 1252(2), 1265(2), 1294(2), 1309(2), 1345(1), 1375(3), 1388(3), 1429(4), 1456(4), 1668(8), 2872(1), 2920(3), 2947(1), 2967(3), 3016(4), 3087(5).

Estimation of the intensities of the three-membered ring frequency (1192 cm^{-1}) and of the double-bond frequency (1668 cm^{-1}) indicate that the ratio of the bromide with a three-membered ring to the unsaturated bromide is about 2:1, which agrees satisfactorily with the unsaturation as determined from the bromine number.

Structure of the bromide. 10 grams of the bromide were mixed in a small flask with 16 g of silver acetate and 5 ml of glacial acetic acid. The mixture was then refluxed at 118-120° for 6 hours. The reaction products were diluted with water and then extracted with ether after the silver bromide had been filtered out. The ether solution was desiccated with calcium chloride, the ether driven off, and the remaining oil distilled at 141-145°.

The resulting ester was hydrogenated, without further purification, at room temperature above a platinum catalyst. When no more hydrogen was added, the ester was saponified for 12 hours with an aqueous solution of potash. The alcohol with a b.p. of 132-136° recovered after the ester had been saponified was dehydrogenated to an aldehyde at 420° above a catalyst (ZnS deposited on pumice).

The resultant aldehyde produced a silver mirror with ammoniacal silver nitrate. It formed two products with 2,4-dinitrophenylhydrazine. One of them, which was only slightly soluble in alcohol, had a m.p. of 139-141° and proved to be a derivative of acetylcyclopropane. The mixed melting point with the 2,4-dinitrophenylhydrazone prepared from pure acetylcyclopropane exhibited no depression.

The second crystalline product was freely soluble in alcohol and had a m.p. of 98° after several recrystallizations; this agrees with the melting point of the 2,4-dinitrophenylhydrazone of normal valeraldehyde.

It formed a crystalline precipitate with a m.p. of 94-99° when reacted with dimedon; this is somewhat lower than the figure given in the literature for normal valeraldehyde (104.5°).

α-Chloroethylcyclopropane. 10 grams of methylcyclopropylcarbinol were treated with 6 g of PCl_3 under the same conditions as those utilized to produce the bromide.

The chloride was a nearly colorless oil with a rather pleasant fragrance. The chloride distilled without residue at 100-103° and 755 mm. Some hydrogen chloride was observed evolving during this distillation. An unsaturated hydrocarbon was formed. Redistillation of the chloride yielded about 1 g of a hydrocarbon fraction with a b.p. of 42-43°. The small amount of the hydrocarbon made it impossible to identify it. A liquid bromide was produced when it was reacted with bromine, which excludes the possibility of its being piperylene, which might have been formed as the result of the splitting out of hydrogen chloride paralleled by the cleavage of the cyclopropane ring. The yield of the chloride with a b.p. of 100-103° (755 mm) was 83% of the theoretical.

d_4^{20} 0.9348; n_D^{20} 1.43362; MR_D 29.08; Calc. 27.95.

The exaltation of 1.13 was somewhat higher than the value for a three-membered ring and was caused by the formation of unsaturated compounds in consequence of the splitting off of HCl.

0.2033 g subs.: 0.2484 g AgCl (Carius). 0.2498 g subs.: 0.3029 g AgCl. Found %: Cl 30.22, 30.00. C_5H_9Cl. Calc. %: Cl 33.96.

Determination of the bromine number indicated that the chloride contained 17-18.5% of unsaturated compounds.

Raman spectrum: 274(3), 310(3), 335(3), 386(10)*, 457(2), 493(3), 533(2), 558(1), 598(1), 638(3), 658(10), 762(5), 821(5), 971(1), 986(1), 1015(1), 1029(2), 1091(1), 1106(1), 1139(1), 1163(1), 1191(8), 1215(1), 1243(3), 1299(3), 1393(4), 1420(2), 1456(2), 1640(1), 1659(1), 2872(1), 2929(4), 2967(1), 3013(5), 3072(5), 3083(4).

Comparison of the intensities of the three-membered ring and double-bond frequencies gave an unsaturation value that agreed satisfactorily with the unsaturation as determined from the bromine number.

The vinylcyclopropane was prepared by the Demyanov method [4], the initial substance used being acetylcyclopropane, which was converted into an oxime. The oxime was reduced to an amine with sodium in absolute alcohol. The amine was then methylated exhaustively. The hydrocarbon was prepared by decomposing the fully substituted free base. The hydrocarbon yields were almost quantitative in this phase of the reaction.

The hydrocarbon was distilled above metallic sodium. Its boiling point at 752 mm was 40.0-40.4°. It was redistilled, the fraction with a b.p. of 40.2-40.4° being collected and then identified.

d_4^{20} 0.7202; d_4^{18} 0.7227; n_D^{20} 1.4139; n_D^{15} 1.4166; MR_D 23.59; Calc. 22.62.

Figures in the literature: as given by Demyanov [4], b.p. 40-40.2° at 755 mm; d_4^{18} 0.7230; n_D^{15} 1.4172; as given by Volkenburgh and associates [17], b.p. 40-41°.

The exaltation (0.97) somewhat exceeds the increment for a three-membered ring and may be due to the "conjugation" of the double bond with the three-membered ring.

Vinylcyclopropane colors tetranitromethane yellow.

Ozonolysis of vinylcyclopropane. 1 gram of the hydrocarbon was dissolved in anhydrous chloroform. Ozonation was performed with dry-ice chilling. After the ozonolysis products had been decomposed with water, they were found to contain formaldehyde, formic acid (determined by the calomel method), and cyclopropylformaldehyde. The 2,4-dinitrophenylhydrazone of the latter had a m.p. of 180-182°. (This m.p. is given as 182-185° in the literature [17]).

The Raman spectrum of the hydrocarbon is given in the table.

Splitting HCl out of α-chloroethylcyclopropane. 15 grams of the chloride were added from a dropping funnel to a solution of 16 g of KOH in 85 ml of ethyl cellosolve heated to boiling [18]. The resulting highly volatile reaction products passed through the reflux condenser (through which there circulated water at a temperature of 50°) without condensing. The vapors entered a well-chilled coil, where they condensed and were collected in a receiver chilled to -20°. The yield of the hydrocarbon was 4.3 g or 40% of the theoretical. A total of 16 g of the substance was synthesized.

The hydrocarbon had a boiling point of 40.5 - 42.5°, most of it distilling at 41°. A test for halogen was negative. It colored tetranitromethane orange.

d_4^{20} 0.7163; n_D^{20} 1.40668; MR_D 23.35; Calc. 22.62. Exaltation 0.73.

0.8 gram of the hydrocarbon was subjected to ozonolysis. The products of the decomposition of the ozonide with water included formaldehyde and acetaldehyde (positive iodoform test). Reaction with 2,4-dinitrophenylhydrazine yielded a mixture of hydrazones with a m.p. of 147 - 149°. We were unable to isolate individual products from the mixture. Determination of the mixed melting points proved that this mixture consisted of the 2,4-dinitrophenylhydrazone of acetaldehyde and the 2,4-dinitrophenylhydrazone of cyclopropylformaldehyde.

1.14 gram of the hydrocarbon was hydrogenated with a platinum catalyst, the solvent employed being alcohol. The hydrogen consumption was 460 ml (0° and 760 mm), constituting an excess of 22.7% over the quantity calculated for a single double bond.

Bromine was added to 3.5 g of the hydrocarbon until the color no longer vanished (12.5 g). The bromide was washed with soda and with water and desiccated with calcium chloride. When distilled, more than half of the bromide passed over at 83 - 85° (18 mm). Its refractive index was n_D^{20} 1.5400, which is the figure for vinylcyclopropane dibromide. The residue in the distilling flask crystallized, the crude crystals weighing 4 g. The crystals had a m.p. of 114.5° after double recrystallization from alcohol. The mixed melting point with piperylene tetrabromide exhibited no depression. The quantity of the crystalline tetrabromide was approximately equivalent to 1/4 of the initial hydrocarbon consisting of piperylene, which agreed with the hydrogenation data.

The Raman spectrum of the hydrocarbon is listed in the table.

SUMMARY

1. A study has been made of the products of the reaction of PBr_3 and PCl_3 with methylcyclopropylcarbinol.

2. It has been shown that most of the α-bromoethylcyclopropane (about 70%) is converted into 5-bromopentene-2.

3. It has been found that α-chloroethylcyclopropane suffers only negligible ring cleavage. Its synthesis and refining involve the partial splitting out of hydrogen chloride (10-15%), yielding vinylcyclopropane.

4. Vinylcyclopropane has been synthesized and its Raman spectrum photographed.

5. A study has been made of the splitting of hydrogen chloride out of α-chloroethylcyclopropane. It has been shown that this yields a hydrocarbon

mixture containing about 75% of vinylcyclopropane and about 25% of trans-piperylene.

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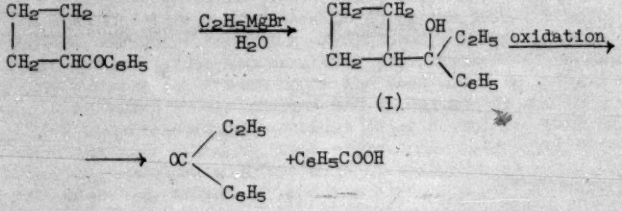
THE REACTION OF ETHYLPHENYLCYCLOBUTYLCARBINOL WITH HYDROCHLORIC AND SULFURIC ACIDS

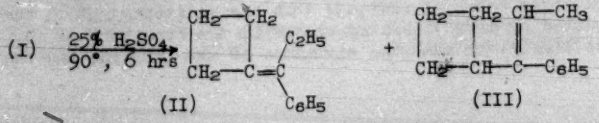
T.A.Favorskaya and I.P Yakovlev

In our previous two reports [1,2] we investigated the reaction of diisopropylcyclobutylcarbinol and methylphenylcyclobutylcarbinol with dilute hydrochloric and sulfuric acids and with concentrated sulfuric acid. We found that the methylphenylcyclobutylcarbinol was merely dehydrated, yielding two isomeric unsaturated hydrocarbons: as-phenylcyclobutylethylene and methylphenylmethylenecyclobutane. The reaction of diisopropylcyclobutylcarbinol with the acids was somewhat more complicated. The reactions with dilute hydrochloric and sulfuric acids produced, in addition to a dehydration product, an isomerization product of the alcohol: 1,1-diisopropylcyclopentanol-2. A similar secondary alcohol is also produced in the organomagnesium synthesis of the tertiary alcohol. When reacted with 35% hydrochloric acid, diisopropylcyclobutylcarbinol is dehydrated and isomerized to a cyclic alcohol with a five-membered ring and to a chloride with and without an isopropyl group shifted from the 1,1 position to the 1,2 position. Only small quantities of the latter products are secured, however.

The present paper deals with the reaction of ethylphenylcyclobutylcarbinol with hydrochloric and sulfuric acids. The ethylphenylcyclobutylcarbinol was synthesized from cyclobutyl phenyl ketone and ethylmagnesium bromide, the yield being 93.5%. Part of the alcohol was oxidized at 65 - 70° with a chromic acid mixture. Oxidation yielded ethyl phenyl ketone and benzoic acid, more than half of the alcohol subjected to oxidation being recovered unchanged. All analogous alcohols containing a cyclobutyl radical seem to exhibit this difficult oxidizability.



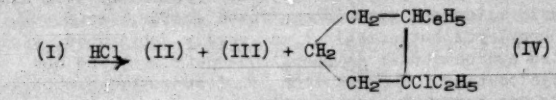
When ethylphenylcyclobutylcarbinol was reacted with 25% sulfuric acid, nearly all of it was converted into a mixture of two unsaturated hydrocarbons after 6 hours of heating to 90°; the mixture consisted of 25% of ethylphenylmethylenecyclobutane and 75% of 1-methyl-2-phenyl-2-cyclobutylethylene, based on the overall yield of 90 - 95%.



Carefull oxidation of this hydrocarbon mixture yielded acetic and succinic acids; the ketones produced were ethyl phenyl ketone and cyclobutyl phenyl ketone:

$$\text{(II), (III)} \xrightarrow[H_2O]{KMnO_4} (CH_2COOH)_2 + CH_3COOH + C_4H_7COC_6H_5 + C_2H_5COC_6H_5.$$

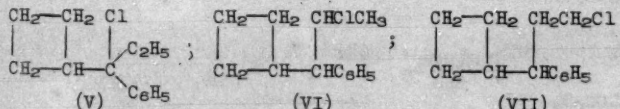
When ethylphenylcyclobutylcarbinol was heated to 90° with 18% hydrochloric acid, the reaction followed three paths, half of the alcohol being recovered unchanged after 6 hours of heating, though the reaction was complete when heating lasted 12 hours; it then yielded 60% of ethylphenylmethylenecyclobutane, some 20% of 1-methyl-2-cyclobutyl-2-phenylethylene, and about 20% of a chloride that was the same as the chloride produced when we used 37% HCl. The reaction proceeded as follows:



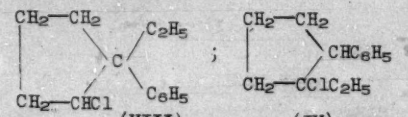
Oxidizing the hydrocarbon mixture produced in the reaction with HCl yielded ethyl phenyl ketone, cyclobutyl phenyl ketone, acetic acid, and succinic acid.

When the alcohol was reacted with 37% hydrochloric acid, deeply chilling the reaction mixture at first (snow and salt) and then gradually raising the temperature to room temperature with effective stirring, the reaction involved the formation of some 40% of 1-methyl-2-phenyl-2-cyclobutylethylene and some 30% of 1-chloro-1-ethyl-2-phenylcyclopentane, less ethylphenylmethylenecyclobutane being produced (approximately 30%). All three products were isolated in the individual state to some extent after prolonged rectification.

The sole distinctive feature was that the chloride exhibits the same relative dispersion as the original alcohol. This seemed to indicate that the chloride was a tertiary one (V) and retained its four-membered ring But in view of the fact that the chloride was returned unchanged when it was heated with anhydrous sodium ethylate, it appeared that it was either secondary (VI, VIII) or primary (VII).



(V) (VI) (VII)



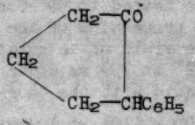
(VIII) (IV)

We did not possess the equipment for determining its structure without subjecting the substance to isomerization. The chloride was distilled above metallic sodium in order to split out HCl. The resulting hydrocarbon differed substantially from those secured with the HCl and H_2SO_4 acids. Its relative dispersion of 30.8, for instance, indicated that this unsaturated hydrocarbon did not contain a four-membered ring (ω_{FCD} 35.0, 35.5), but rather a five or a six-membered ring. This seems to indicate that the splitting out of the HCl was either accompanied by a far reaching change in the structure of the molecule (which is most likely) or that the structure of the chloride was that of

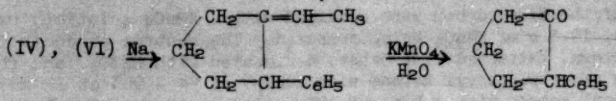
(IV), (which is less likely) though the action of the sodium ethylate did not split out HCl elements because of the screening of the ethyl and phenyl groups.

The relative dispersion ω_{FCD} of the substances prepared from the methyl-, ethyl-, and isopropylphenylcyclobutylcarbinols is given by the following experimental figures: 1) 27.3 for alcohols containing a cyclobutyl radical; 2) 35.8 for unsaturated hydrocarbons with a cyclobutyl radical; 3) 30.5. for unsaturated hydrocarbons containing a five-membered ring; and 4) 23.6 for chlorides containing a five-membered ring; 5) it ought to be 27.3 for chlorides that contain a cyclobutyl radical.

Oxidizing the hydrocarbon with a $KMnO_4$ solution yielded a compound containing a carbonyl group. Its semicarbazone had a m.p. of 214° with decomposition. Analysis for nitrogen yielded 18.62% and 18.33% nitrogen, instead of the 19.35% called for on the assumption that the semicarbazone had been prepared from 2--phenylcyclopentanone (IX).


(IX)

Hence the problem of the chloride's structure is still unresolved. Inasmuch as the chemical findings support the existence of a secondary chloride (VI, VIII), the physical findings supporting the structures (V), (VI), or (VII), while the results of oxidizing the hydrocarbon prepared from the chloride support (IV) or (VI), we must assume that the chloride was either a secondary one (VI) or a tertiary one (IV) and that the reactions in which the HCl was split out and oxidation took place were as follows:



EXPERIMENTAL

Synthesis of ethylphenylcyclobutylcarbinol. A solution of 70 g of ethyl bromide in 150 ml of absolute ether was added a drop at a time to a chilled and rapidly stirred mixture of 14 g of magnesium chips and 50 ml of absolute ether. After the magnesium had dissolved, 90 g of cyclobutyl phenyl ketone in 75 ml of absolute ether were added to the resultant organomagnesium compound. The reaction mass was stirred for 2 more hours and then allowed to stand until the following day, after which it was chilled and decomposed by adding pieces of ice. The ethereal layer was decanted, the residue being decomposed with dilute (1:4) hydrochloric acid and then extracted with ether. The ether extract was washed with a soda solution, combined with the bulk of the ethereal layer, and desiccated with $MgSO_4$. The ether was driven off and the alcohol distilled, the yield being 100 g, or 93.5% of the theoretical. The alcohol was a slightly mobile, transparent liquid with the odor of camphor. A test for a double bond with a soda solution of $KMnO_4$ was negative.

B.p. 127 - 128° at 10 mm; n_D^{21} 1.5302; ω_{FCD} 26.8; d_4^0 1.0255. d_4^{21} 1.0085; MR_D 58.21; Calc. 57.92.
0.0655 g substance: 0.1965 g CO_2; 0.0562 g H_2O; 0.1270 g substance: 0.3814 g CO_2; 0.1048 g H_2O. 0.0387 g substance; 16.60 g benzene: Δ t 0.061°; 0.0610 g substance; 16.60 g benzene: Δ t 0.102° Found %: C 81.99, 81.85; H 9.60, 9.23. M 192.3, 181.5. $C_{13}H_{18}O$. Calculated %: C 82.10 H 9.47. M 190.0.

Oxidation of ethylphenylcyclobutylcarbinol. 50 grams of $K_2Cr_2O_7$, 60 g of K_2SO_4 (1.84), and 200 ml of H_2O were used in oxidizing 10 g of the alcohol. The alcohol was added drop by drop to the chromic acid mixture heated to 55°, the temperature of the mixture being raised to 65° after all the alcohol had been added and kept at that temperature for 3.5 hours. Then the reaction mixture was cooled and diluted with 200 ml of water, and the reaction product was extracted with ether. The ether extract was washed with alkali and with 50 ml of water and then desiccated with $MgSO_4$. Driving off the ether and fractionating the residual oil yielded 5.4 g of the original alcohol and 1.9 g of ethyl phenyl ketone. The latter was converted into a semicarbazone with a m.p. of 181°. The mixed melting point of the latter with the semicarbazone of the known substance exhibited no depression. The acid portion of the reaction products yielded benzoic acid with a m.p. of 120°, confirmed by a mixed melting point test.

Reaction of ethylphenylcyclobutylcarbinol with sulfuric acid. 15 grams of the alcohol were heated to 90° for 6 hours with 15 ml of 25% sulfuric acid. Appropriate processing of the reaction product yielded nothing but a nearly quantitative yield of an unsaturated hydrocarbon. The hydrocarbon had a b.p. of 238 - 242° at 759 mm after double distillation above metallic sodium. It was a mobile liquid with the odor of pine tar.

B.p. 108 - 110° at 10 mm; $n_D^{19.5}$ 1.5470; ω_{FCD} 34.9; d_4^0 0.9723; $d_4^{19.5}$ 0.9570; MR_D 57.00; Calc: 56.41.
0.0818 g substance: 0.2722 g CO_2; 0.0694 g H_2O; 0.0762 g substance: 0.2520 g CO_2; 0.0586 g H_2O. 0.0327 g substance; 15.60 g benzene: Δ t 0.064°; 0.0680 g substance; 15.60 g benzene: Δ t 0.130°. Found %: C 90.70, 90.27; H 9.49, 8.62. M 164.9, 168.5. $C_{13}H_{16}$. Calculated %: C 90.59; H 9.41. M 172.0.

6.5 grams of the hydrocarbon were oxidized with a $KMnO_4$ solution; oxidation was not vigorous, 19.5 g of $KMnO_4$ being consumed. The neutral products were distilled with steam, extracted with ether, desiccated with $MgSO_4$, and fractionated. This yielded 1 g of ethyl phenyl ketone with a b.p. of 94 - 96° at 12 mm plus 3 g of cyclobutylphenyl ketone with a b.p. of 125 - 134° at 12 mm. The ketones yielded semicarbazone with melting points of 176 and 182°, respectively. The mixed melting points of the semicarbazones with the equivalent known derivatives exhibited no depression. The acid part distilled after acidulation yielded acetic acid, while the residue that was left after distillation yielded succinic acid with a m.p. of 180°. Its mixed melting point with known succinic acid exhibited no depression.

Found %: Ag 64.43, 64.49. $C_2H_3O_2Ag$. Calculated %: Ag 64.67.

Reaction of ethylphenylcyclobutylcarbinol with 18% hydrochloric acid. 15 grams of the alcohol were heated for 12 hours with 20 ml of 18% hydrochloric acid to the boiling point of the solution. The reaction product was extracted with ether, desiccated with $MgSO_4$, and distilled, three fractions being collected (at 12 mm): I) 104 - 115°, 9.1 g; II) 115 - 134°, 1.9 g; and III) 134 - 138°, 2.4 g. The intermediate Fraction II was not analyzed further.

Fraction III was a chloride, which was combined with the identical chloride prepared by the action of the 37% HCl. Fraction I was an unsaturated hydrocarbon - a colorless, highly mobile liquid with the odor of fresh spruce oil. The hydrocarbon had the following constants after having been double distilled above metallic sodium:

B.p. 237 - 241° at 759 mm; B.p. 107 - 110° at 10 mm; $n_D^{19.5}$ 1.5475; ω_{FCD} 35.6; d_4^0 0.9737; $d_4^{19.5}$ 0.9578; MR_D 57.12; Calc. 56.41.

0.1151 g substance: 0.3809 g CO_2; 0.0943 g H_2O; 0.1251 g substance: 0.4142 g CO_2; 0.1064 g H_2O. 0.0450 g substance; 16.45 g benzene: Δt 0.082; 0.0505 g substance; 16.45 g benzene: Δt 0.090. Found %: C 90.40, 90.25; H 9.17, 9.52. M 167.8, 171.7. $C_{13}H_{16}$. Calculated %: C 90.59; H 9.41. M 172.0.

Oxidation of the $C_{13}H_{16}$ hydrocarbon secured with the 18% hydrochloric acid. 25.3 grams of $KMnO_4$ were consumed for 8 g of the hydrocarbon. The neutral products were distilled with steam, yielding 3.8 g of ethyl phenyl ketone with a b.p. of 95 - 97° at 14 mm and 1.2 g of cyclobutyl phenyl ketone with a b.p. of 125 - 133° at 14 mm. The semicarbazones of these ketones had melting points of 177 and 182°, respectively, and their mixed melting points with the corresponding known semicarbazones exhibited no depression.

After acidulation, steam distillation of the acid part yielded acetic acid, while the residue yielded oxalic acid with a m.p. of 184.5°. Its mixed melting point with known oxalic acid exhibited no depression.

Found %: Ag 63.98. $C_2H_3O_2Ag$. Calculated %: Ag 64.67.

Reaction of ethylphenylcyclobutylcarbinol with 37% hydrochloric acid. 30 grams of the alcohol were poured into 400 ml of 37% hydrochloric acid, very efficiently stirred, and chilled with a snow-and-salt freezing mixture. The reaction mass was stirred under the stated conditions for 12 hours, left to stand overnight without stirring, and then stirred for 6 hours at room temperature. Then the reaction product was extracted with ether, washed with 30 ml of water, desiccated with $MgSO_4$, and fractionated, the following three fractions being collected at 6.5 mm: I) 102 - 104°, 9.6 g; II) 104.5 - 111°, 9.3 g; and III) 125 - 130°, 8.2 g.

Most of Fraction I consisted of ethylphenylmethylenecyclobutane, with a trace of 1-methyl-2-phenyl-2-cyclobutylethylene. The ethylphenylmethylenecyclobutane was a colorless, highly mobile liquid with the odor of the hydrocarbon produced by reacting the alcohol with dilute hydrochloric acid. The hydrocarbon had the following constants after having been double distilled over sodium.

B.p. 234 - 238° at 754 mm; B.p. 107 - 109° at 10 mm; n_D^{19} 1.5470; ω_{FCD} 35.0; d_4^0 0.9664; d_4^{19} 0.9500; MR_D 57.36; Calc: 56.41.
0.0520 g substance: 16.40 g benzene: Δt 0.094°; 0.0582 g substance; 16.40 g benzene: Δt 0.110°. Found: M 170.2, 162.5. $C_{13}H_{16}$. Calculated: M 172.0.

The bulk of Fraction II consisted of 1-methyl-2-cyclobutyl-2-phenylethylene, with a trace of ethylphenylmethylenecyclobutane. The 1-methyl-2-cyclobutyl-2-phenylethylene was a colorless, highly mobile liquid with the odor of the hydrocarbon produced by reacting the alcohol with sulfuric acid. The hydrocarbon had the following constants after having been double distilled above sodium:

B.p. 237 - 239°at 754 mm; B.p. 108 - 110° at 10 mm; n_D^{19} 1.5515; ω_{FCD} 35.3; d_4^0 0.9746; d_4^{19} 0.9589; MR_D 57.27; Calc: 56.41.
0.0359 g substance; 16.75 g benzene: Δt 0.064; 0.0725 g substance; 16.35 g benzene: Δt 0.136 Found: M 168.8, 164.5. $C_{13}H_{16}$. Calculated: M 172.0.

Fraction III was a chloride. The chloride was secured, after repeated fractional distillations, as a slightly mobile, barely yellowish liquid with a pine odor.

B.p. 128 - 130° at 7.5 mm; $n_D^{18.5}$ 1.5448; ω_{FCD} 27.6; 1.0812; $d_4^{18.5}$ 1.0680; MR_D 61.70; Calc: 61.73.
0.1311 g substance: 0.0889 g AgCl; 0.1692 g substance: 0.1154 g AgCl.
0.0381 g substance; 16.35 g benzene: Δt 0.060; 0.709 g substance; 16.35 g benzene: Δt 0.136. Found %: Cl 16.77, 16.87. M 195.5, 191.8. $C_{13}H_{17}Cl$. Calculated %: Cl 17.03, M 208.5.

Splitting HCl out of the $C_{13}H_{17}Cl$ chloride. 9 grams of the chloride were heated to 100° with 22 g of sodium ethylate for 5 hours, but no splitting out occurred, the chloride being recovered with the same physical constants as before. Then it was double-distilled above sodium, 8 g of the chloride yielding 4.6 g of an unsaturated, colorless, highly mobile hydrocarbon.

B.p. 235 - 245° at 762 mm; B.p. 104 - 109° at 10 mm; n_D^{20} 1.5364; ω_{FCD} 30.8; d_4^0 0.9715; d_4^{20} 0.9568; MR_D 56.09; Calc: 56.41.
0.1011 g substance: 0.3359 g CO_2; 0.0892 g H_2O; 0.1073 g substance: 0.3524 g CO_2; 0.0881 g H_2O. 0.0438 g substance; 15.70 g benzene: Δt 0.087°; 0.0848 g substance; 15.70 g benzene: Δt 0.161°. Found %: C 90.50, 90.24; H 9.83, 9.19. M 168.5, 161.2. $C_{13}H_{16}$. Calculated %: C 90.59; H 9.41. M 172.0.

Oxidation of the hydrocarbon $C_{13}H_{16}$. 12.8 g of $KMnO_4$ was gradually added, as de-oxidation progressed, to 4.2 g of the hydrocarbon in 100 ml of water. The oxidation products were found to include oxalic acid (m.p. 185°) and benzoic acid (m.p. 119.5°). Their mixed melting points with the respective known acids exhibited no depression. We also secured 2.1 g of 2-phenylcyclopentanone. The semicarbazone of this ketone had a m.p. of 214° with decomposition.

0.0912 g substance: 14.35 ml N_2 (21°, 761 mm); 0.0809 g substance: 13.00 ml N_2 (21°, 761 mm). Found %: N 18.33, 18.62. $C_{12}H_{15}ON_3$. Calculated %: N 19.35.

SUMMARY

1. Ethylphenylcyclobutylcarbinol and the products of its dehydration and isomerization by sulfuric and hydrochloric acids have been synthesized for the first time.

2. Reacting the alcohol with 25% H_2SO_4 at 90° converts 25% of it into ethylphenylmethylenecyclobutane (II) and 75% into 1-methyl-2-phenyl-2-cyclobutylethylene (III).

3. Reacting the alcohol with 18% HCl converts it into the hydrocarbons (II) (60%) and (III) (20%) and the chloride (IV). The structure of the chloride (IV) has not been rigorously proved, but its distillation above sodium and subsequent oxidation of the resulting hydrocarbon yielded a compound whose semicarbazone had a composition resembling that of the derivative of phenylcyclopentanone-2.

The mean arithmetical values of the relative dispersion ω_{FCD} are given for some alcohols containing a cyclobutyl radical, and for their dehydration, isomerization, and substitution products.

LITERATURE CITED

[1] T.A.Favorskaya and I.P.Yakovlev, J.Gen. Chem, 22, 113 (1952).[1])

[2] T.A.Favorskaya and I.P.Yakovlev, J. Gen. Chem, 22, 122 (1952).[2])

The A.E.Favorsky Laboratory of the
A.A.Zhdanov State University of
Leningrad, Awarded the Order of Lenin.

Received August 28, 1952.

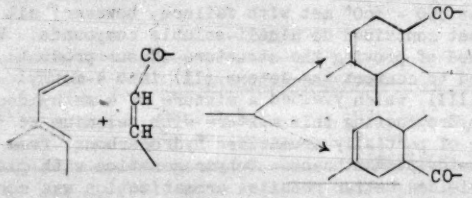
1) See Consultants Bureau English translation, p. 133.

2) See Consultants Bureau English translation, p. 143.

130. SYNTHESIS OF POLYCYCLIC COMPOUNDS. VIII. CONDENSATION OF 1-VINYL-Δ^1-CYCLOHEXENE WITH Δ^1-CYCLOHEXENONE

I.N.Nazarov, I.V.Torgov, and M.V.Kuvarzina

During the past few years our laboratory has worked out syntheses of polycyclic compounds and steroids involving the condensation of cyclic dienes with α,β-unsaturated cyclic ketones. Once the problem of the synthesis itself had been successfully resolved [1], the question of establishing the structure of the synthesized compounds arose. When cyclic dienes such as 1-vinyl-Δ^1-cyclohexene or 1-vinyl-Δ^1-octalin are condensed with α,β-unsaturated cyclic ketones, two structural isomers may result, depending on the orientation of the molecules during the diene synthesis:

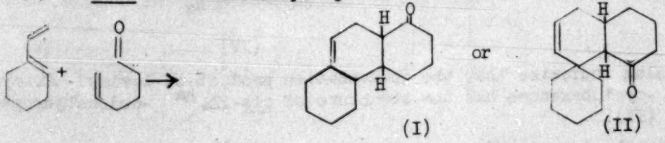


We were greatly interested in learning what structures predominate in each case and how they are affected by the formation of various substitutents and functional groups within the molecule of the cyclic diene and the unsaturated ketone.

The objective of the present research was condensing 1-vinyl-Δ^1-cyclohexene with Δ^1-cyclohexenone and establishing the structure of the resulting tricyclic ketone of the phenanthrene series. Here it is much easier to convert the condensation product into known compounds than in the condensation of cyclic dienes with cyclopentenones [1].

It should be noted that there are no examples in the literature up to now of the rigorous proof of the structure of the tricyclic isomers produced by condensing dienes with unsaturated ketones, as has been pointed out recently in a monograph on diene synthesis [2].

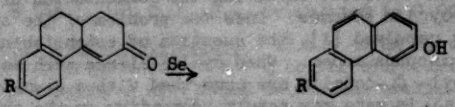
It is comparatively easy to condense 1-vinyl-Δ^1-cyclohexene with Δ^1-cyclohexenone, the condensation yielding more than 40% of a crystalline tricyclic ketone, to which we may assign the structure of <u>cis</u>-Δ^{8a}-dodecahydrophenanthren-1-one (I) or <u>cis</u>-Δ^{8a}-dodecahydrophenanthren-4-one (II).



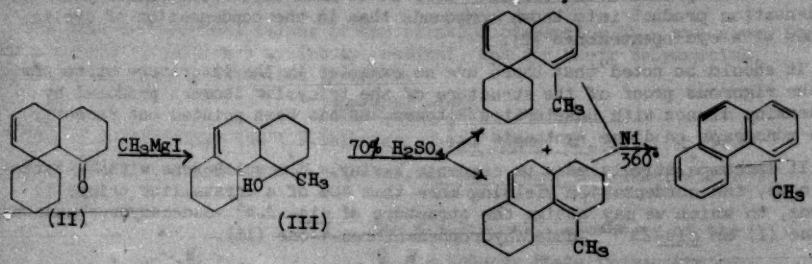
(I) (II)

As will be shown below, the product proved to be the dodecahydrophenanthrene (II), the isomer (I) being either wholly absent from the condensation products or else being present in negligible quantity (not over 10%).

The surest way of establishing the structure was, no doubt, converting the ketone (II) into an aromatic compound, one of the derivatives of phenanthrene, which have been investigated extensively. We were attracted at first to the simplest method of aromatization: the direct dehydrogenation of the ketone (II) to the corresponding phenanthrol, especially as data has been recently published on the successful dehydrogenation of ketones of this type [3]:



All our attempts to dehydrogenate the ketone (II) with selenium at 320 - 340° or with Raney's nickel at 350 - 360° met with failure, however; all we got was a mixture of products that contained no alkali-soluble compounds. We therefore resorted to another method of proving the structure of our product: methylmagnesium iodide was used to convert the ketone (II) into 4-methyl-Δ^{8a}-dodecahydrophenanthren-4-ol (III), which yielded a mixture of 4-methyldecahydrophenanthrenes (IV). Dehydrogenating this mixture with selenium at 300 - 310° yielded a liquid mixture of partially aromatized hydrocarbons, from which we were unable to isolate methylphenanthrene. Dehydrogenation with platinized charcoal at 330 - 350° yielded better results: aromatization was more complete; the refractive index of the resulting products rose substantially (n_D^{20} 1.61 as against 1.55 - 1.57 for the products of selenium dehydrogenation); and a small amount of a picrate with a m.p. of 132 - 135°, as against 141° for the picrate of 4-methylphenanthrene, was secured from the resulting products. Dehydrogenation with Raney's nickel at 350 - 360° proved to be even more successful. We again secured a liquid mixture of hydrocarbons, but when we treated it with picric acid, we readily produced the picrate of 4-methylphenanthrene, from which we secured the 4-methylphenanthrene (V) itself.



(II) (III) (IV) (V)

The foregoing indicates that the condensation product of 1-vinyl-Δ-cyclohexene and Δ-cyclohexenone has the structure of cis-Δ^{8a}-dodecahydrophenanthren-4-one (II).

We were greatly interested in converting the cis ketone (II) into the corresponding trans compound, as this would be of importance in synthesizing compounds related to the steroids, in which rings of trans configuration

predominate. Instances of this sort of transformation are fairly numerous among bicyclic compounds [7]. We recently effected similar cis-trans conversions in our laboratory, using 6-methoxy-Δ^6-octalone-1 and 1,6-diketodecalin, likewise synthesized in diene condensations.

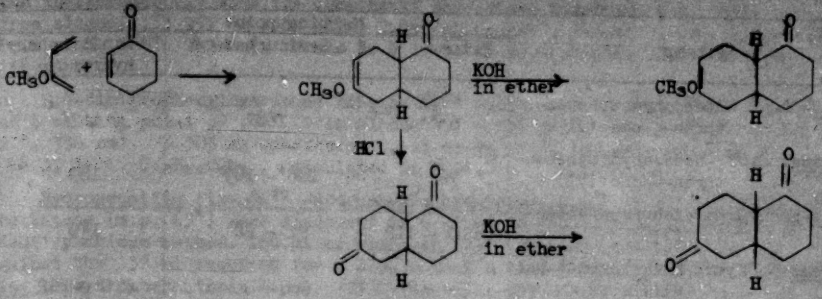
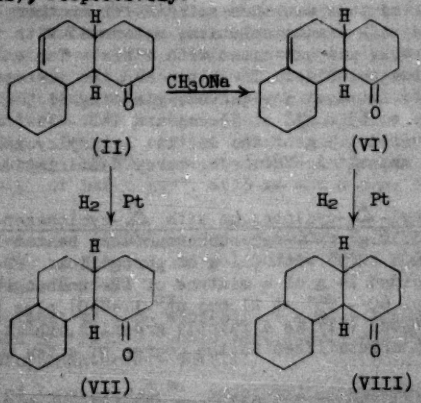


TABLE 1

Melting point	4-methylphenanthrene		1-methylphenanthrene
	Prepared by us	Described in the literature	
Hydrocarbon	41°	49 - 50°	118°[4]; 117 - 118°[6];
Picrate	141 - 142	140 - 141	123[5]; 135 - 136[4];
Styphnate	134	135	139[5]; 149 - 150[4].

We have investigated the action of sodium methylate upon cis ^{8a}-dodecahydrophenanthren-4-one (II) and found that the cis ketone (II) was smoothly converted into the trans ketone (VI). Hydrogenation of the cis and trans isomers yielded cis-perhydrophenanthren-4-one (VII) and trans-perhydrophenanthren-4-one (VIII), respectively:



(II) (VI) (VII) (VIII)

The melting points of these ketones and of their derivatives are listed in Table 2.

TABLE 2

Ketones	Melting point		
	Ketone	Semicarbazone	Dinitrophenylhydrazone
Cis-Δ^{8a}-dodecahydrophenanthren-4-one (II)	63°	188°	167°
Trans-Δ^{8a}-dodecahydrophenanthren-4-one (VI)	76	188 - 189	189
Cis-perhydrophenanthren-4-one (VII)	110 - 112	91 - 92	140
Trans-perhydrophenanthren-4-one (VIII)	74 - 75	-	210 - 212

These examples indicate that diene condensation with α,β-unsaturated cyclic ketones yields polycyclic ketones with only cis configurations. An analogous rule for the formation of cis compounds in diene syntheses has been put forward previously [8].

EXPERIMENTAL

The Δ'-cyclohexenone was prepared by a method developed in our laboratory, involving splitting hydrogen bromide out of α-bromocyclohexanone; its constants were: b.p. 71° at 25 mm; n_D^{18} 1.4840.

The 1-vinyl-Δ'-cyclohexene was prepared by dehydrating 1-vinyl-1-cyclohexanol with potassium bisulfate, as described by I.N.Nazarov and T.D.Nagibina [1], and also by dehydration utilizing phosphoric anhydride as described below.

Dehydration of 1-vinylcyclohexan-1-ol with phosphoric anhydride. 10 grams of phosphoric anhydride were added in small portions during the course of 45 minutes, with stirring, to 20 g of 1-vinylcyclohexan-1-ol (b.p. 62° at 9 mm; n_D^{18} 1.4770) in 100 ml of anhydrous acetone. The temperature of the reaction mixture rose to 35°. The mixture was then stirred for another half-hour at 50°, and then neutralized with a soda solution, saturated with potash until the liquid separated into layers, and extracted with ether. The ether extract was desiccated with calcium chloride. The ether and the acetone were driven off, and the residue was fractionated at low vacuum, yielding 11.5 g of 1-vinyl-Δ'-cyclohexene, with a b.p. of 63 - 65° at 53 mm; and 142 - 144° at 760 mm; n_D^{21} 1.4910. We also recovered 1.5 g of the initial 1-vinylcyclohexan-1-ol with a b.p. of 62 - 63° at 10 mm; n_D^{21} 1.4780. The tarry distillation residue totaled 2.5 g.

Condensation of 1-vinyl-Δ'-cyclohexene with Δ'-cyclohexenone. 7 grams of vinyl-Δ'-cyclohexene and 16 g of Δ'-cyclohexenone were heated in a metal ampoule for 3 hours to 200 - 205° with 0.1 g of pyrogallol. Fractionation of the reaction products yielded 14 g of a mixture of the unchanged cyclohexenone and vinylcyclohexene (b.p. 60 - 65° at 21 mm; n_D^{20} 1.4840) plus 6 g of cis-Δ^{8a}-dodecahydrophenanthren-4-one (II) as a faintly greenish, thick liquid with a pleasant fragrance, which crystallized in the course of a few minutes into minute needles.

B.p. 127° at 3 mm; n_D^{20} 1.5280; m.p. 63° (from alcohol). 4.910 mg substance: 14.760 mg CO_2; 4.280 mg H_2O; 4.270 mg substance: 12.840 mg CO_2; 3.780 mg

H_2O. Found %: C 82.0, 82.1; H 9.75, 9.9. $C_{14}H_{20}O$. Calculated %: C 82.35; H 9.8.

The semicarbazone of cis-Δ^{8a}-dodecahydrophenanthren-4-one was thrown down instantaneously when the components were mixed together. B.p. 188° (from alcohol). 3.992 mg substance: 0.549 ml N_2 (24°, 742mm). 3.640 mg substance: 0.506 ml N_2 (25°, 741 mm). Found %: N 15.4, 15.5. $C_{15}H_{23}ON_3$. Calculated %: N 16.1.

2,4-dinitrophenylhydrazone of cis-Δ^{8a}-dodecahydrophenanthren-4-one had a melting point of 167° (from alcohol). 3.098 mg substance: 0.386 ml N_2 (21°, 736 mm). 3.303 mg substance: 0.413 ml N_2 (21°, 736 mm). Found %: N 14.1, 14.1. $C_{20}H_{24}O_4N_4$. Calculated %: N 14.6.

Hydrogenating cis-Δ^{8a}-dodecahydrophenanthren-4-one (II). 1.1 grams of the ketone (m.p. 63°) were dissolved in 5 ml of alcohol and hydrogenated by Adams' platinum method. 160 ml of hydrogen (23°, 752 mm) were absorbed, as against the 132 ml required for a single double bond. This yielded 0.9 g of cis-perhydrophenanthren-4-one (VIII) as colorless crystals with a m.p. of 110 - 112° (from alcohol).

4.460 mg substance: 13.375 mg CO_2; 4.195 mg H_2O. Found %: C 81.8; H 10.5. $C_{14}H_{22}O$. Calculated %: C 81.5; H 10.7.

The semicarbazone of cis-perhydrophenanthren-4-one (VII) had a m.p. of 91 - 92° (from 50% methanol).

3.997 mg substance: 0.567 ml N_2 (24°, 735 mm). 3.902 mg substance: 0.539 ml N_2 (23°, 753 mm). Found %: N 15.8, 15.8. $C_{15}H_{25}ON_3$. Calculated %: N 16.0.

The 2,4-dinitrophenylhydrazone of cis-perhydrophenanthren-4-one (VII) had a m.p. of 140° (from alcohol).

3.891 mg substance: 0.504 ml N_2 (20°, 745 mm). 3.298 mg substance: 0.428 ml N_2 (20°, 745 mm). Found %: N 14.9, 14.95. $C_{20}H_{26}O_4N_4$. Calculated %: N 14.5.

Action of methylmagnesium iodide upon cis-Δ^{8a}-dodecahydrophenanthren-4-one (II). 5 grams of cis-Δ^{8a}-dodecahydrophenanthren-4-one (II), with a m.p. of 63°, were dissolved in 10 ml of absolute ether and then added to a methylmagnesium iodide solution, prepared from 1.2 g of magnesium and 7 g of methyl iodide in 40 ml of absolute ether. The reaction mass was stirred for three hours at 20° and then allowed to stand overnight. The next day the mass was stirred for six hours at 35°, cooled, and decomposed with 30 ml of 10% sulfuric acid. The ether layer was separated, and the aqueous layer extracted with ether, after which the combined ether extracts were washed with a hyposulfite solution and desiccated with sodium sulfate. Driving off the ether and distilling the product in vacuo yielded 3 g of 4-methyl-Δ^{8a}-dodecahydrophenanthren-4-ol (III) as colorless crystals with a b.p. of 140 - 142°, at 3 mm and a m.p. of 117 - 118° (from 75% alcohol).

3.820 mg substance: 11.486 mg CO_2; 3.620 mg H_2O. 5.090 mg substance: 15.307 mg CO_2; 4.852 mg H_2O. Found %: C 82.0, 82.1; H 10.6, 10.7. $C_{15}H_{24}O$. Calculated %: C 81.8; H 10.9.

In this experiment we also secured 1.4 g of a liquid fraction with a b.p. of 132° at 5 mm and n_D^{20} 1.5260, which most likely was the impure original cis-Δ^{8a}-dodecahydrophenanthren-4-one (II).

Dehydration of 4-methyl-Δ^{8a}-dodecahydrophenanthren-4-ol (III). A mixture of 3.0 g of the carbinol, with a m.p. of 117 - 118°, and 5 ml of 70% sulfuric acid

was stirred vigorously for three hours at 75°. After the product had been neutralized with soda, extracted with ether, and desiccated, and the ether driven off, the residue of 4-methyldecahydrophenanthrenes (IV) was double-distilled in vacuo, yielding: Fraction I, b.p. 114 - 117° at 3 mm, 0.5 g; and Fraction II, b.p. 125 - 127° at 3 mm, 1.0 g.

Fraction I was a colorless, mobile liquid with a faint odor.

n_D^{20} 1.5245; d_4^{20} 0.9681; MR_D 63.8; Calc. 63.8

8.21 mg substance: 26.77 mg CO_2; 8.19 mg H_2O. Found %: C 89.0; H 11.2. $C_{15}H_{22}$. Calculated %: C 89.1; H 10.9.

Fraction II was a colorless, mobile liquid: n_D^{20} 1.5260; d_4^{20} 0.9776; MR_D 64.4; Calc. 63.8.

7.31 mg substance: 23.80 mg CO_2; 7.20 mg H_2O. Found %: C 88.9; H 11.1. $C_{15}H_{22}$. Calculated %: C 89.1; H 10.9.

Dehydrogenation of the mixture of 4-methyldecahydrophenanthrenes (IV) using selenium. 0.8 grams of the substance (Fraction II) was placed in a small Wurtz flask together with 2.0 g of selenium and heated to 300 - 310° for three hours. Hydrogen selenide was evolved. After the mixture had cooled, the product was extracted with ether, the ether driven off, and the residue distilled in vacuo. This yielded 0.4 g of a substance with a b.p. of 127 - 135° at 3 mm; n_D^{20} 1.5490. When the substance was mixed with an alcoholic solution of picric acid, a minute quantity of the picrate settled out (m.p. 87 - 94°).

When the dehydrogenation was prolonged, the refractive index of the reaction products rose to n_D 1.57, though the yield dropped off. No distillable products were secured even when dehydrogenation was continued for 15 hours. A test using Fraction I yielded similar results.

Dehydrogenation of the mixture of 4-methyldecahydrophenanthrenes (IV) using platinized charcoal. 1.5 grams of the substance and 0.7 g of finely powdered platinized charcoal (30% Pt) were placed in a small Wurtz flask and heated to 330 - 350° in a gentle current of carbon dioxide. The hydrogen evolved was led off to an azotometer that contained a solution of potassium hydroxide. Practically no more hydrogen was evolved after five hours of heating. A total of 580 ml of hydrogen (18°, 760 mm) was evolved, as against the 850 mm called for theoretically. After the reaction mass had cooled, it was extracted with ether, the ether driven off, and the residue distilled in vacuo.

Fraction I, b.p. 133 - 135° at 3mm, 0.2 g; n_D^{20} 1.5450; Fraction II, b.p. 136 - 144° at 3 mm, 0.1 g; n_D^{20} 1.5825; Fraction III, b.p. 145 - 150° at 3 mm, 0.5 g; n_D^{20} 1.6145; residue 0.5 g.

Fractions I and II did not produce a picrate. We managed to secure a small quantity (less than 0.5 g) of a picrate with a m.p. of 132 - 135° from Fraction III.

Dehydrogenation of the mixture of 4-methyldecahydrophenanthrenes (IV) using Raney nickel. 2.2 grams of the mixture of methyldecahydrophenanthrenes, 100 ml of benzene, and 10 g of Raney nickel, washed successively with alcohol, ether, and benzene, were placed in a half-liter rotating autoclave and heated in an atmosphere of nitrogen to 350 - 360° for 3.5 hours and to 370 - 380° for 30 minutes. The benzene solution was filtered, the benzene driven off, and the residue distilled in vacuo: Fraction I, b.p. 80 - 120° at 1 mm, 0.7 g; Fraction II, b.p. 120 - 130° at 1 mm, 1.0 g; and a tarry residue of about 0.4 g.

Neither Fraction I nor Fraction II crystallized upon cooling. Fraction II was mixed with a solution of 1 g of picric acid in 10 ml of absolute alcohol. An orange-colored picrate was thrown down at once. The picrate was allowed to stand three hours on ice, after which it was suction-filtered and washed three times with cold alcohol. This yielded 0.6 g of the picrate with a m.p. of 135 - 140°. Another 0.1 g of the picrate was secured from the mother liquor. Crystallization of the 0.6 g of the picrate from 2 ml of alcohol yielded 0.4 g of a substance with a m.p. of 141 - 142° that remained unchanged after further crystallization.

The picrate was decomposed by agitating a solution of 0.35 g of the picrate in 50 ml of ether with a 2 - 3% solution of sodium hydroxide. A second agitation with a fresh portion of the alkali yielded a wholly colorless ether layer. After desiccation with sodium sulfate and driving off the ether, the residue of 0.17 g crystallized completely into a slightly yellowish crystalline mass with a m.p. of 39 - 41°. Crystallization from 2 ml of methanol yielded 0.1 g of 4-methylphenanthrene (V) as pliant white needles with a m.p. of 41°.

8.30 mg substance: 28.55 mg CO_2; 4.70 mg H_2O. 5.82 mg substance: 20.07 mg CO_2; 3.17 mg H_2O. Found %: C 93.9, 94.1; H 6.35, 6.0. $C_{15}H_{12}$. Calculated %: C 93.7, H 6.3.

Treating Fraction I with picric acid yielded only a negligible quantity of picrate.

The picrate of the synthesized 4-methylphenanthrene (V) had a m.p. of 141 - 142°. The styphnate had a sharp melting point of 134°. The dehydrogenation experiment was performed with both Fractions I and II of the mixture of methyldecahydrophenanthrenes (IV), the picrate of 4-methylphenanthrene being obtained in both instances.

Attempt to dehydrogenate cis-Δ^{8a}-dodecahydrophenanthren-4-one (II) using selenium. 1.7 grams of the ketone (II) and 1.5 g of selenium were heated to 320 - 340° in a 10 ml Wurtz flask for four hours. The liquid boiled at first, but boiling practically ceased toward the end of the heating period. The residue was dissolved in 20 ml of ether and mixed with 20 ml of 5% potassium hydroxide for an hour. The aqueous layer was separated, extracted with ether, and acidulated. Nothing but a minute amount of tar was secured.

Isomerizing cis-Δ^{8a}-dodecahydrophenanthren-4-one (II) to the trans isomer (VI). A solution of 0.5 g of cis-Δ^{8a}-dodecahydrophenanthren-4-one (II), with a m.p. of 63°, in 5 ml of methanol that contained 0.5 % of sodium methylate was refluxed for three hours. The product was neutralized with acetic acid, the methanol was driven off in vacuo, and the residue was diluted with 5 ml of water and extracted with ether. Driving off the ether left behind a viscous yellow oil that crystallized two days later. Crystallization from alcohol yielded 0.3 g of trans-Δ^{8a}-dodecahydrophenanthren-4-one (VI) with a m.p. of 76°. Its mixed melting point with the original ketone (II) was 41 - 43°.

The semicarbazone of the trans-Δ^{8a}-dodecahydrophenanthren-4-one (VI) had a m.p. of 188 - 189°; its mixed melting point with the semicarbazone of the original ketone (II) was 186 - 188°.

The 2,4-dinitrophenylhydrazone of the trans-Δ^{8a}-dodecahydrophenanthren-4-one (VI) had a m.p. of 189° (from alcohol).

3.198 mg substance: 0.406 ml N_2 (20°, 745 mm). 3.605 mg substance: 0.460 ml N_2 (20°, 745 mm). Found %: N 14.5, 14.6. $C_{20}H_{24}O_4N_4$. Calculated %: N 14.6.

The mixed melting point with the dinitrophenylhydrazone of the original

ketone (II) was approximately 154°.

Hydrogenation of trans-Δ^{8a}-dodecahydrophenanthren-4-one (VI). 0.5 gram of the ketone (VI), with a m.p. of 76°, was dissolved in 5 ml of alcohol and hydrogenated with Pt by the Adams method. 80 ml of hydrogen (23°, 740 mm) were absorbed, the theory calling for 65 ml of hydrogen. Filtration and crystallization from alcohol yielded 0.3 g of trans-perhydrophenanthren-4-one (VIII) with a m.p. of 74 - 75°. Its mixed melting point with a sample of the cis isomer was 61 - 62°.

The 2,4-dinitrophenylhydrazone of trans-perhydrophenanthren-4-one (VIII) had a m.p. of 210-212° (from alcohol).

2.205 mg substance: 0.286 ml N_2 (20°, 745 mm). 3.904 mg substance: 0.502 ml N_2 (20°, 752 mm). Found %: N 14.9, 14.8. $C_{20}H_{28}O_4N_4$. Calculated %: N 14.5.

SUMMARY

1. Condensing 1-vinyl-Δ'-cyclohexene with Δ'-cyclohexenone yields cis-Δ^{8a}-dodecahydrophenanthren-4-one (II), the structure of which has been proved by a series of transformations, ending up with the well-known 4-methylphenanthrene (V). If the other isomeric ketone (I), i.e., cis-Δ^{8a}-dodecahydrophenanthren-1-one is formed in this condensation at all, it cannot total more than 10% of the whole.

2. Cis-Δ^{8a}-dodecahydrophenanthren-4-one (II) has been isomerized to trans-Δ^{8a}-dodecahydrophenanthren-4-one (VI) by using sodium methylate.

3. The cis- and trans-perhydrophenanthren-4-ones (VII and VIII) have been synthesized by hydrogenating the cis- and trans-Δ^{8a}-dodecahydrophenanthren-4-ones (II and VI).

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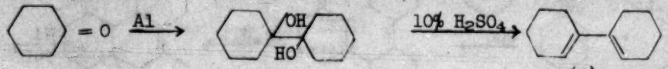
131. SYNTHESIS OF POLYCYCLIC COMPOUNDS. IX. CONDENSATION OF DI-Δ'-CYCLOHEXENYL WITH α,β-UNSATURATED CYCLIC KETONES

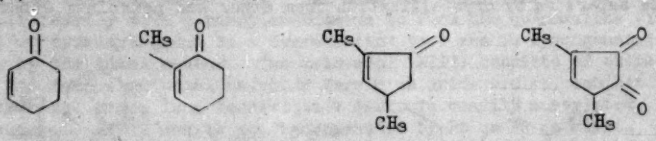
I.N.Nazarov and I.V.Torgov

Pursuing our researches on the synthesis of polycyclic compounds by the method of diene condensation with α,β-unsaturated cyclic ketones, we decided to ascertain whether it was feasible to perform this reaction with bicyclic and tetracyclic dienes, both of whose double bonds were in the rings. As a typical example of a bicyclic diene we selected di-Δ'-cyclohexenyl (I), which can be readily prepared from cyclohexanone by reducing the latter to a pinacone and dehydrating:



(I)

The ability of di-Δ'-cyclohexenyl to enter into a diene condensation has been established by Barnett and Lowrens [1], who condensed it with maleic anhydride and p-benzoquinone, as well as by Gruber and Adams [2], who condensed di-Δ'-cyclohexenyl with acrolein. It was important to find out whether di-Δ'-cyclohexenyl was able to condense with α,β-unsaturated cyclic ketones, which react with much more difficulty, as we had ascertained in a number of earlier investigations [3], than maleic anhydride and the aliphatic α,β-unsaturated aldehydes and ketones. In order to determine this we explored the condensation of dicyclohexenyl (I) with Δ'-cyclohexenone (II), 1-methyl-Δ'-cyclohexen-6-one (III), 1,3-dimethyl-Δ'-cyclopenten-5-one (IV), and 1,3-dimethyl-Δ^3-cyclopenten-4,5-dione (V):



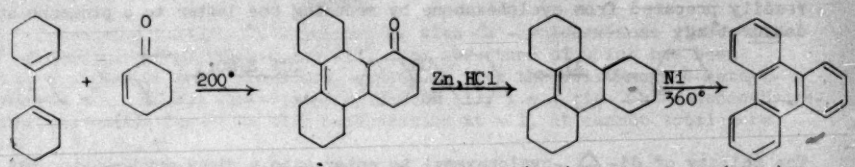
(II) (III) (IV) (V)

We found that dicyclohexenyl (I) reacts at approximately 200° with all three unsaturated cyclic ketons (II, III, and IV), yielding the respective tetracyclic ketones, the yields ranging from 10 to 30%. The cyclohexenone (II), which has no substituents, reacts most easily with dicyclohexenyl (I), the methylcyclohexenone (III), which has a methyl group attached to a double bond, reacting less readily. Though it possesses a methyl group attached to the double bond, the dimethylcyclopentenone (IV) reacts almost as easily with the dicyclohexenyl (I) as the cyclohexenone (II), which has no substituents. The reaction rate and the condensation product yield drop off when the temperature is lowered below 200°.

The dimethylcyclopentendione (V), which is more actively dienophilic than the α,β-unsaturated cyclic ketones, reacts with the dicyclohexenyl (I) even at 100°.

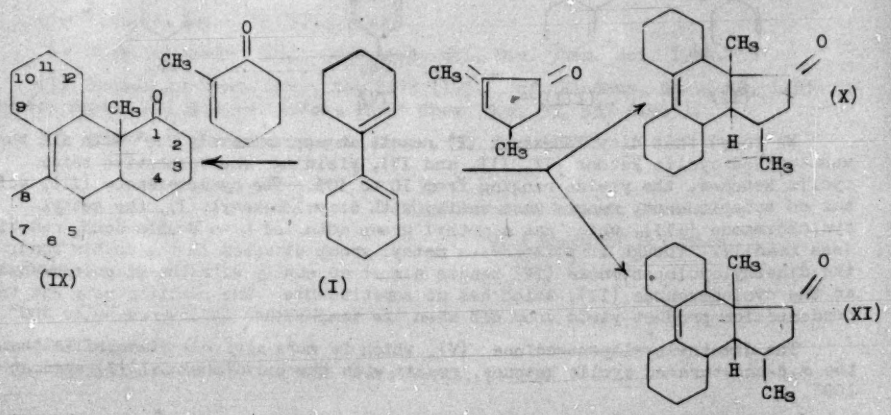
In contrast to the syntheses effected in our laboratory in the past [3], where we had to use an excess of the cyclic ketone to diminish the dimerization of the diene, this excess is unnecessary in the present instance, inasmuch as dicyclohexenyl (I) does not dimerize even at 200°. This circumstance also facilitated the isolation of the condensation products in the pure state.

Heating equimolecular quantities of dicyclohexenyl (I) and Δ^{1}-cyclohexenone (II) to 200° for 6 hours produced Δ^{8a}-hexadecahydrotriphenylen-1-one (VI), the yield being about 30%, based on the diene used for the reaction. The ketone (VI) was converted into Δ^{8a}-hexadecahydrotriphenylene (VII) by the Clemmensen method, the compound (VII) then yielding the well-known triphenylene (VIII) when dehydrogenated with Raney's nickel. The melting points of the last hydrocarbon, as well as that of its picrate, agreed with the figures given in the literature [4].



(I) (II) (VI) (VII) (VIII)

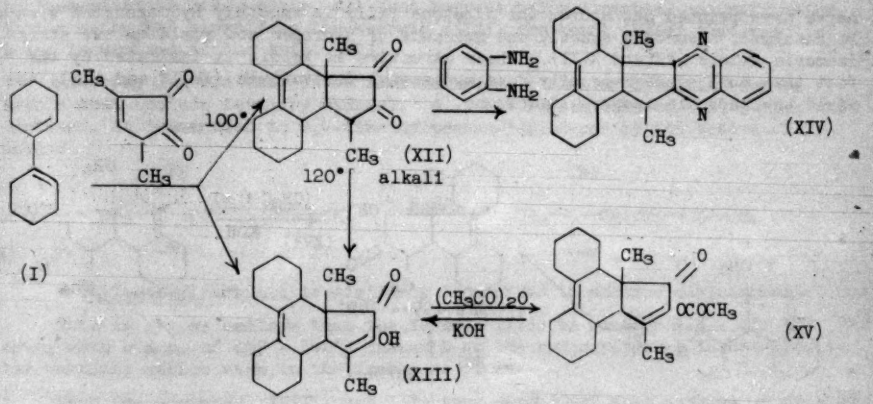
The yield of 12b-methyl-Δ^{8a}-hexadecahydrotriphenylen-1-one (IX) was only 10%, based on the diene used for the reaction, when the dicyclohexenyl (I) was condensed with 1-methyl-Δ^{1}-cyclohexen-6-one (III), despite the prolonging of the reaction time (27 hours at 200°). The dimethylcyclopentenone (IV) reacted with the dicyclohexenyl (I) more readily, 6 hours at 200° yielding about 30% of 3,8-dimethyl-Δ^{5}-dodecahydro-4,5,6,7-dibenzindan-1-one, which was isolated as two stereo isomers (α,β), to which we assigned the structures (X) and (XI). They could be separated by crystallization from ether and petroleum ether.



(IX) (I) (X) (XI)

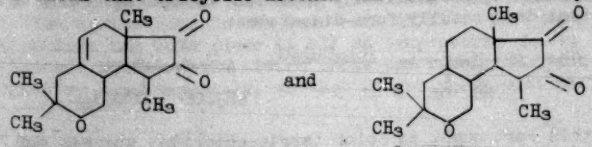
Under ordinary conditions neither ketone (X) nor ketone (XI) can be hydrogenated, no matter whether a platinum or a palladium catalyst is employed; this

is due to the peculiar position of the double bond, belong to three rings in the condensed system. Condensing the dicyclohexenyl (I) with 1,3-dimethyl- - Δ^1-cyclopenten-4,5-dione (V) at 100° produced a 60% yield of 3,8-dimethyl- - Δ^5-dodecahydro-4,5,6,7-dibenzindan-1,2-dione (XII). Raising the temperature a little bit, (to 120°) no longer yields the diketone (XII), but rather its isomerization product, 3,8-dimethyl- $\Delta^{2,5}$-decahydro-4,5,6,7-dibenzindan-2-ol-1- -one (XIII). This isomerization takes place with extraordinary ease, also occurring quantitatively when alkaline agents (caustic alkalies, piperidine) act upon the diketone (XII). Acid agents do not cause the reverse transformation.



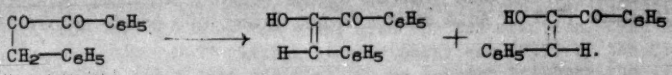
The structure of the diketone (XII) and of the keto-enol (XIII) follow from their physical and chemical properties. The diketone (XII) consists of yellow crystals that react readily with o-phenylenediamine to form the quinoxaline (XIV), which exhibits no hydroxyl group in a Tserevitinov test and is hydrogenated with a Pt catalyst by the Adams method. The keto-enol (XIII) consists of white crystals; it does not form a quinoxaline, color ferric chloride violet, exhibit the presence of one hydroxyl group in a Tserevitinov test, is readily acetylated, yielding the monoacetate (XV), and is not hydrogenated by Pt or Pd catalysts, although it contains two double bonds. It should be added that enols are hard to hydrogenate. Nor can the simplest analog of the keto-enol (XIII), viz: 3,5-dimethyl- - Δ^2-cyclopenten-2-ol-1-one, be hydrogenated with Pt or Pd catalysts.

That enol forms of cyclic 1,2-diketones exist has been known for a long time. A recent quantitative determination [5] has shown that 1,2-cyclopentandione and 1,2-cyclohexandione are 100% enolic. In one of our previous papers we have shown that tricyclic ketones that contain a tetrahydropyran ring:

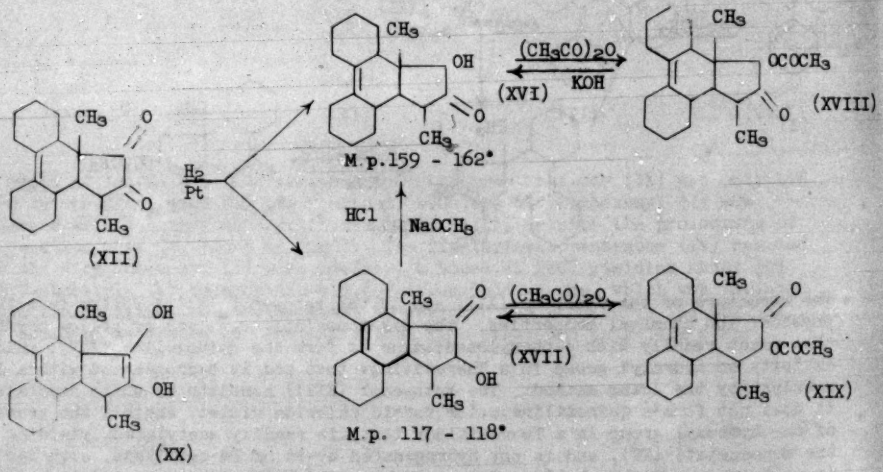


likewise exist only in the enolic form [6].

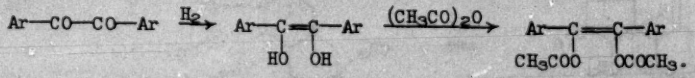
In the present research, however, we encounter the interesting fact that the 1,2-diketone (XII) is stable, though it is very easily converted into the keto-enolic form (XIII). We have found only one similar instance in the literature of the existence of both a 1,2-diketone and of the respective keto--enol. Phenylbenzylglyoxal readily yields two keto-enolic forms (cis and trans), one of which has been isolated in the pure state [7].



As we have pointed out above, the diketone (XII) is smoothly hydrogenated with a Pt catalyst, absorbing exactly one molecule of hydrogen and yielding two stereo-isomeric ketols (XVI and XVII). Their structure as ketols is indicated by the fact that both of them readily form monoacetyl derivatives (XVIII and XIX), and yield the same dinitrophenylhydrazone.



Tserevitinov determinations of the hydroxyl groups in the ketols (XVI and XVII) yielded figures that were close to 2 (1.7 - 1.8), and we first thought that we had the ene-diol (XX). But then we should secure one product instead of a mixture of isomers. Likewise, an ene-diol of that sort ought to yield a diacetyl derivative readily, while no carbonyl derivatives (dinitrophenylhydrazone) should be produced at all. Fuson [8] produced many ene-diols by hydrogenating aromatic diketones and showed that they readily form diacetates:

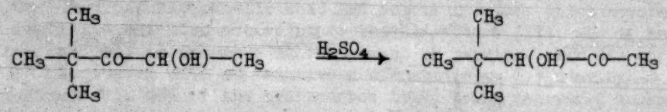


Lastly, ene-diols of this sort ought to color ferric chloride, whereas our compounds did not.

We can only assume that the keto groups in the ketols (XVI) and (XVII) are

enolized with extraordinary ease and behave like hydroxyl groups when acted upon by a Grignard reagent. The acetates (XVIII) and (XIX) likewise exhibit a single hydroxyl group in a Tserevitinov determination, so that they, too, can be enolized by methylmagnesium iodide. The production of the same dinitrophenylhydrazone from each of the ketols (XVI and XVII) indicates that the one ketol is isomerized to the other under the conditions prevailing during the formation of the dinitrophenylhydrazone, i.e., in an acid medium. As a matter of fact, when the low-melting ketol (XVII) is acted upon by hydrochloric acid, it is isomerized to the high-melting ketol (XVI). Sodium methylate effects the same irreversible isomerization in the cold. When the acetate of the low-melting ketol (XIX) is acted upon by hydrochloric acid, no isomerization takes place, all that happens being a partial saponification. Sodium methylate saponifies the acetate (XIX), the ketol (XVII) that results being isomerized to the ketol (XVI).

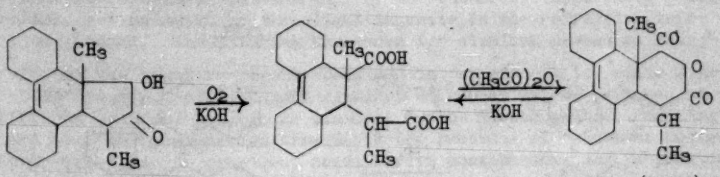
Favorsky and his associates have described a similar izomerization of ketols that contain tertiary radicals [9]. 4,4-Dimethylpentan-2-ol-3-one, for instance, is isomerized to 4,4-dimethylpentan-3-ol-2-one by the action of acids:



Methylbenzoylcarbinol is similarly isomerized to phenylacetylcarbinol.

This is why we believe that the formula (XVI) is more probable for the ketol with a m.p. of 159 - 162°, inasmuch as the hydroxyl group is attached to the tertiary carbon atom in the instances cited.

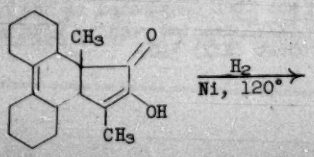
When the acetates (XVIII) and (XIX) were saponified with alkali, we secured the dibasic acid (XXI). Further research indicated that this acid can be secured from the ketols (XVI) and (XVII) themselves by oxidizing them with atmospheric oxygen in an alkaline solution. Treating the acid (XXI) with acetic anhydride yields the anhydride (XXII):



XVI (or XVII) (XXI) (XXII)

In order to produce the ketol (XVII) in some other manner we tried to hydrogenate the double bond in the keto-enol (XIII). We found, however, that hydrogenation does not take place at all at temperatures below 100°, in an autoclave with Raney's nickel, while at 120° both the double bond and the keto group are hydrogenated simultaneously, so that we get the glycol (XXIII).

(XIII)

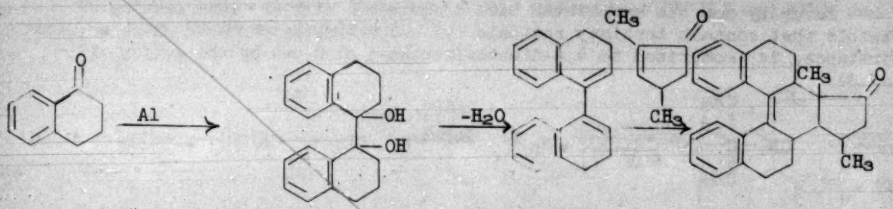


(XXIII)

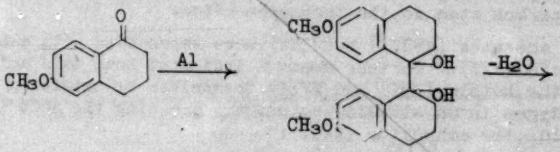
Hydrogenating the high-melting ketol (XVI) yielded a noncrystallizing mixture of products, from which we were unable to isolate the glycol (XXIII).

It should be said that the double bond linking three condensed rings remained untouched in every case of hydrogenation.

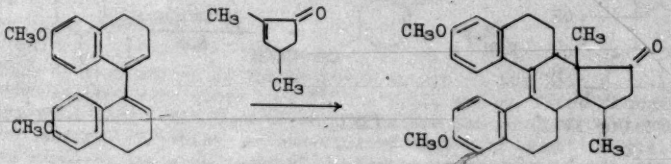
After we had established the condensability of di-Δ^1-cyclohexenyl (I) with α,β-unsaturated cyclic ketones, it was only natural to apply this reaction to the tetracyclic dienes, which can be prepared by reducing bicyclic ketones to pinacones and dehydrating the latter. If the initial ketones contained functional groups, this should finally yield polycyclic compounds that contained the estrone system. The polycyclic ketone (XXVI) ought to be produced from α-tetralone, while 6-methoxytetralone ought to yield the polycyclic dimethoxy ketone (XXIX) containing the methyl ester of estrone:



(XXIV) (XXV) (XXVI)

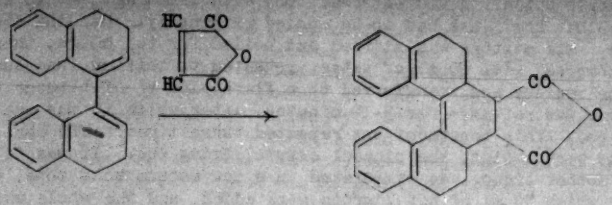


(XXVII)



(XXVIII) (XXIX)

We chose α-tetralone as the first substance to be tested. The α-tetralone was reduced with aluminum in a mixture of alcohol and benzene, thus converting it into a pinacol (XXIV), which was then dehydrated to the corresponding hydrocarbon (XXV). This hydrocarbon (XXV) reacted readily with maleic anhydride, yielding the normal addition product (XXX) [10].



(XXV) (XXX)

All our attempts to condense the hydrocarbon (XXV) with 1,3-dimethyl-Δ^1-cyclopenten-5-one (IV) met with failure, however; at 200° the bulk of the hydrocarbon (XXV) was recovered unchanged, while raising the temperature caused substantial tarring, though even then part of the hydrocarbon did not enter into the reaction. Adding chloroacetic acid and sulfur dioxide, which accelerate the diene synthesis reaction according to the literature [11], was of no use: all that happened was an increase in the amount of tarring. Nor did the hydrocarbon (XXV) react even with so reactive a dienophile as 1,3-dimethyl-Δ^1-cyclopenten-4,5-dione (V), 80% of the hydrocarbon (XXV) being recovered unchanged at 120°.

The situation was even more difficult as far as 6-methoxytetralone was concerned. When we reduced this compound with aluminum in an alcohol-benzene mixture, we obtained a difficultly separable mixture of products that contained the pinacol (XXVII). Treating this mixture with acetic acid did not yield the pure diene (XXVIII) as stated in the literature [12], but a mixture of low-melting substances from which we were unable to isolate any individual substance.

We also explored the reduction of α-decalone and 9-methyl-Δ^6-octalone-1. We found that these ketones could not be reduced by aluminum in benzene at all, while in an alcohol-benzene mixture part of the ketone was apparently reduced to a carbinol, as indicated by the slight increase in the refractive index of the reaction product. Substituting magnesium for aluminum caused no change.

In view of the negative results obtained in our efforts to reduce α-decalone and 9-methyl-Δ^6-octalone-1 with aluminum or magnesium, we explored the possibility of securing polycyclic pinacols by the Karash method: reacting the ketones with methylmagnesium bromide in the presence of cobaltous chloride. This method, which yields excellent results with benzophenone and isophorone [13], proved to be wholly useless for cyclohexanone and α-decalone, the usual reaction involving the formation of a tertiary alcohol taking place. Thus, α-decalone and 9-methyl-Δ^6-octalone-1 do not yield pinacols by any of the most commonly used reduction methods.

EXPERIMENTAL

Reduction of cyclohexanone to a pinacol. 25 grams of aluminum granules and 200 ml of absolute benzene were placed in a three-necked flask fitted with a reflux condenser, a calcium chloride tube, and a stirrer with a mercury seal. The benzene was heated almost to the boiling point and stirred while a solution of 12 g of mercuric chloride in 100 g of freshly distilled cyclohexanone was

added in a single batch. A violent reaction, with frothing, set in within 1 or 2 minutes, so that the flask had to be cooled externally. Boiling stopped 20 minutes later. The mixture was stirred and boiled for two hours, then chilled with ice, decomposed with 80 ml of water, reheated to boiling, and suction-filtered. The residue was transferred to a flask, 100 ml of benzene were added, and the mixture was refluxed for 5-10 minutes, after which it was again hot-suction-filtered. This treatment was repeated three times. The combined benzene solutions were cooled, the pinacol crystallizing out. It was filtered out, and the mother liquor was evaporated in a low vacuum to a total volume of 100 ml, after which 50 ml of hot ligroin were added, and the whole was set aside to crystallize. The yield of the pinacol with a m.p. of 123-124° totaled 38 g. Recrystallization raised the m.p. to 128°, but this purification is unnecessary for its subsequent use. Approximately 2 g more of the pinacol may be secured by fractionating the mother liquor and crystallizing the fraction with a b.p. of 100-130° at 2 mm.

Dehydration of the pinacol. 40 grams of the pinacol with a m.p. of 123-124° and 200 ml of 10% sulfuric acid were stirred together for four hours while heated on a boiling water bath. The oily layer was separated, and the aqueous layer was extracted with 30 ml of benzene. The benzene extract was combined with the oily layer, and the whole was desiccated with calcium chloride and then distilled. This yielded 29 g of di-Δ^1-cyclohexenyl (I) with a b.p. of 95-96° at 3 mm; n_D^{20} 1.5335. The yield was 89%.

Condensation of di-Δ^1-cyclohexenyl (I) with Δ^1-cyclohexenone (II). We found, in special experiments, that the reaction was slow at 185°, the diene undergoing no change even when it was heated to 200° by itself.

A mixture of 6.1 g of the dicyclohexenyl (I) and 3.5 g of cyclohexenone (II) (b.p. 66° at 22 mm; n_D^{20} 1.4830) was heated for 6 hours to 200° in a sealed ampoule filled with carbon dioxide. Fractionation yielded the following results: Fraction I: b.p. 50-55° at 9 mm - 0.7 g; Fraction II: b.p. 50-70° at 1 mm - 2.6 g; Fraction III: b.p. 70-150° at 1 mm - 0.5 g; Fraction IV: b.p. 150-158° at 1 mm - 3.1 g; and a residue of about 3 g.

The bulk of Fraction II consisted of the unreacted dicyclohexenyl. Fraction IV was diluted with 5 ml of ether. Crystals began to settle out after a few hours had passed, their quantity increasing when the solution was chilled. This yielded 1.0 g of Δ^{8a}- hexadecahydrotriphenylen-1-one (VI) with a m.p. of 97-99°. Crystallization from a small quantity of petroleum ether yielded beautifully shaped white crystals of the ketone (VI) with a m.p. of 99-100°, the m.p. being unaffected by further recrystallization.

10.95 mg subs.: 33.52 mg CO_2; 10.23 mg H_2O. 8.92 mg subs.: 27.29 mg CO_2; 8.38 mg H_2O. Found %: C 83.5, 83.5; H 10.5, 10.5. $C_{18}H_{26}O$. Calc. %: C 83.7; H 10.1.

The dinitrophenylhydrazone, which was produced with extraordinary ease, consisted of golden needles (from benzene) with a m.p. of 211-212° (corr.).

5.645 mg subs.: 0.614 ml N_2 (24°, 733 mm). 5.680 mg subs.: 0.626 ml N_2 (23°, 732 mm). Found %: N 12.1, 12.2. $C_{24}H_{30}O_4N_4$. Calc. %: N 12.8.

When the mother liquor left after the ketone (VI) was crystallized out was treated with dinitrophenylhydrazine, a dinitrophenylhydrazone with the same melting point (211-212°) settled out.

Clemmensen reduction of Δ^{8a}-hexadecahydrotriphenylen-1-one (VI). A mixture of 3.2 g of the ketone (VI), 25 ml of toluene, 30 ml of glacial acetic

acid, 25 ml of fuming hydrochloric acid, and 10 g of amalgamated zinc in fine shavings (treated for an hour with 50 ml of 4% mercuric chloride) was boiled vigorously for 3 hours, after which 15 ml of fuming hydrochloric acid were added and boiling was continued for another 4 hours. The toluene layer was separated, washed with 10% potassium hydroxide and then with water, desiccated with calcium chloride, and filtered, and the solvent was driven off in vacuo. The viscous residue was distilled, yielding 2.1 g of Δ^{8a}-hexadecahydrotriphenylene (VII) as a very viscous liquid with a b.p. of 140-145° at 1.5 mm, which crystallized in part. The crystals had a m.p. of 87-90° after suction filtering and recrystallization from petroleum ether.

10.24 mg subs.: 33.02 mg CO_2; 11.07 mg H_2O. 9.59 mg subs.: 30.87 mg CO_2; 10.32 mg H_2O. Found %: C 88.0, 87.9; H 12.1, 12.0. $C_{18}H_{28}$. Calc. %: C 88.5; H 11.5.

Dehydrogenation of Δ^{8a}-hexadecahydrotriphenylene (VII). 2.0 grams of the hydrocarbon synthesized in the previous experiment, 30 ml of anhydrous technical benzene containing thiophene, and 10 g of Raney's nickel washed with alcohol, ether, and benzene successively, were heated in an atmosphere of nitrogen in a rotating autoclave to 350-355° for 7.5 hours and to 370-380° for 30 minutes. The solution was then filtered and two-thirds of the solvent driven off. As the resultant light bluish-green fluorescing solution cooled, 0.4 g of well-formed, slightly yellowish crystals of triphenylene (VIII) settled out; they had a m.p. of 194-195° (corr.) after having been washed with benzene and dried in a desiccator. The mother liquor yielded another 0.2 g of the same crystals. Crystallization from glacial acetic acid had no effect upon their melting point.

6.551 mg subs.: 22.670 mg CO_2; 3.120 mg H_2O. 3.975 mg subs.: 13.795 mg CO_2; 1.995 mg H_2O. Found %: C 94.4, 94.7; H 5.3, 5.6. $C_{18}H_{12}$. Calc. %: C 94.7; H 5.3.

0.15 gram of the triphenylene was dissolved in 5 ml of chloroform and then mixed with a solution of 0.15 g of picric acid in 3 ml of chloroform. The minute bright-yellow needles of the picrate were thrown down at once. Their melting point was 222-223 (corr.) after washing with chloroform and drying (0.2 g).

According to the literature [4], the melting point of triphenylene is 196-198°, while that of its picrate is 223°.

Condensation of the dicyclohexenyl (I) with 1-methyl-Δ^1-cyclohexen-6-one (III). A mixture of 11.2 g of the methylcyclohexenone (III) (b.p. 60° at 12 mm; n_D^{20} 1.4820) and 15 g of the dicyclohexenyl (I) was heated in an atmosphere of carbon dioxide within a sealed ampoule for 27 hours at 200°. Fractionation yielded the following results:

Fraction I: b.p. 50-53°/8 mm - 4.0 g; Fraction II: b.p. 53°/8 mm - 65°/1.5 mm - 1.0 g; Fraction III: b.p. 65-70°/1.5 mm - 12.0 g; Fraction IV: b.p. 70-150°/1.5 mm - 2.0 g; Fraction V: b.p. 150-155°/1.5 mm - 2.3 g; and a residue of 1.5 g.

Fraction I consisted of the unreacted methylcyclohexenone. The bulk of Fraction III consisted of the unreacted dicyclohexenyl. Fraction V was 12b-methyl-Δ^{8a}-hexadecahydrotriphenylen-1-one (IX). Redistillation of this fraction yielded 1.5 g of the substance as a thick, noncrystallizing glycerol-like liquid.

B.p. 160-163°/2 mm; n_D^{20} 1.5440; d_4^{20} 1.064; MR_D 80.7; Calc. 80.7.

12.41 mg subs.: 38.03 mg CO_2; 11.94 mg H_2O. 14.81 mg subs.: 45.47 mg CO_2; 14.08 mg H_2O. Found %: C 83.6, 83.8; H 10.8, 10.6. $C_{19}H_{28}O$. Cacl. %: C 83.8, H 10.4.

The dinitrophenylhydrazone consisted of yellow, readily soluble crystals (from petroleum ether) with a m.p. of 162-165°.

3.745 mg subs.: 0.404 ml N_2 (19°, 752 mm). 4.052 mg subs.: 0.433 ml N_2 (20°, 752 mm). Found %: N 12.5, 12.3. $C_{25}H_{32}O_4N_4$. Calc. %: N 12.45.

Condensation of the dicyclohexenyl (I) with 1,3-dimethyl-Δ^1-cyclopenten-5-one (IV). A mixture of 10.1 g of the dicyclohexenyl (I), 21.0 g of the dimethylcyclopentenone (IV), and 0.01 g of pyrogallol was heated to 190-195° for 6 hours in an atmosphere of carbon dioxide within a sealed ampoule. Fractionation yielded the following results: Fraction I: b.p. 65°/24 mm - 16.5 g; Fraction II: b.p. 65-82°/2 mm - 4.0 g; Fraction III: b.p. 82-100°/2 mm - 1.5 g; Fraction IV: b.p. 100-150°/2 mm - 0.7 g; Fraction V: b.p. 150-153°/2 mm - 6.5 g; and a residue of 0.5 g.

Fraction I consisted chiefly of the initial dimethylcyclopentenone. Fractions II and III consisted, for the most part, of the dicyclohexenyl. Fraction V was a mixture of the stereo isomers of 3,8-dimethyl-Δ^5-dodecahydro-4,5,6,7-dibenzindan-1-one (X and XI), which gradually crystallized. Successive crystallizations from ether and petroleum ether yielded the high-melting α-isomer (2.0 g), with a m.p. of 102-103°, and the low-melting β-isomer (0.4 g), with a m.p. of 72-73°. We also secured 2.1 g of crystals with a broad melting point (62-70°), which consisted of the contaminated β-isomer. The mixed melting point of the alpha and beta stereo isomers was 59-66°.

The alpha isomer crystallized as large white crystals (from ether) with a m.p. of 102-103°. It is freely soluble in ether and benzene, less so in petroleum ether and in 80% alcohol.

5.100 mg subs.: 15.695 mg CO_2; 4.705 mg H_2O. 7.620 mg subs.: 23.495 mg CO_2; 7.045 mg H_2O. Found %: C 84.0, 84.1; H 10.3, 10.3. $C_{19}H_{28}O$. Calc. %: C 83.8; H 10.4.

The dinitrophenylhydrazone was readily produced by boiling alcoholic solutions of the components with a small quantity of hydrochloric acid for 5 minutes. The yellow crystals (from benzene) had m.p. (decomp.) 246-247° (corrected).

4.204 mg substance: 0.465 ml N_2 (23°, 738 mm). 3.000 mg substance: 0.330 ml N_2 (23°, 738 mm). Found %: N 12.4, 12.3. $C_{25}H_{32}O_4N_4$. Calculated %: N 12.45.

The β-isomer consisted of small irregular prisms. It is freely soluble in ether, petroleum ether, and other solvents.

4.700 mg substance: 14.470 mg CO_2; 4.345 mg H_2O. 6.030 mg substance: 18.545 mg CO_2; 5.525 mg H_2O. Found %: C 84.0, 83.9; H 10.3, 10.3. $C_{19}H_{28}O$. Calculated %: C 83.8, H 10.4.

The dinitrophenylhydrazone was produced by boiling solutions of the components with a small amount of hydrochloric acid for two hours. Beautifully formed yellow crystals (from benzene or alcohol) with a m.p. of 207-208° (corr.). Its mixed melting point with the nitrophenylhydrazone of the alpha isomer was 205-214°.

3.615 mg substance: 0.408 ml N_2 (22°, 753 mm). 4.090 mg substance: 0.464 ml N_2 (23°, 752 mm). Found %: N 12.9, 13.0. $C_{25}H_{32}O_4N_4$. Calculated %: N 12.45.

Condensation of the dicyclohexenyl (I) with 1,3-dimethyl-Δ^1-cyclopentene-4,5-dione (V). a) A mixture of 5.6 g of the dicyclohexenyl (I), 4.3 g of the dimethyl-

cyclopentenedione (V), and 10 ml of anhydrous benzene was heated on a boiling water bath for six hours in an atmosphere of carbon dioxide within a sealed ampoule. The benzene solution was poured into 8 ml of alcohol while still hot. Several hours later the precipitated crystals of the diketone (XII) were suction filtered and washed with cold alcohol. The yellow crystals weighed 4.9 g. Another 1.25 g of large, well-formed crystals were recovered from the mother liquor. The yield of the diketone (XII), with a m.p. of 126-129°, totalled 6.15 g, or 62% of the theoretical. Crystallization from alcohol yielded a wholly pure product (5 g), with the constant melting point of 130-131°. The diketone is freely soluble in dioxane, benzene, and ethyl acetate, less so in alcohol, ether, and acetic acid, and even less so in petroleum ether, while it is insoluble in water.

7.160 mg subs.: 20.850 mg CO_2; 5.800 mg H_2O. 5.280 mg subs.: 15.380 mg CO_2; 4.405 mg H_2O. Found %: C 79.5, 79.5; H 9.1, 9.3. $C_{19}H_{26}O_2$. Calculated %: C 79.7; H 9.15.

In some of the runs we succeeded in isolating minute quantities of the keto-enol (XIII) from the mother liquor as white crystals with a m.p. of 148-150°.

The condensation may also be carried out without using sealed ampoules, but then the flask must be fitted with a reflux condenser, and toluene substituted for the benzene. This does not affect the yield.

The diketone does not give a color reaction with ferric chloride nor does it evolve methane when reacted with methylmagnesium iodide.

b) A mixture of 1.8 g of the dicyclohexenyl (I), 1.4 g of the dimethylcyclopentenedione (V), and 5 ml of benzene was heated to 120° for 4.5 hours in an atmosphere of carbon dioxide within a sealed ampoule. The benzene was then driven off in vacuo, and the remaining viscous yellow liquid crystallized partially by the next day. The crystals were suction-filtered and washed with petroleum ether, yielding 0.3 g of white crystals of the keto-enol (XIII), with a m.p. of 149-151°. We managed to secure 0.1 g of the yellow crystals of the diketone (XII) from the mother liquor their melting point being 125-127° after recrystallization from alcohol, and their mixed melting point with the diketone prepared in the preceding test exhibited no depression.

Condensation of the diketone (XII) with o-phenylenediamine. A solution of 0.3 g of the diketone (XII) and 0.1 g of o-phenylenediamine in 12 ml of glacial acetic acid was boiled for 10 minutes. As the dark-red solution cooled, white crystals of the quinoxaline (XIV) settled out. They were suction filtered, washed with acetic acid, and dried in a desiccator. This yielded 0.2 g of a product with a m.p. of 185-186° (corr.), the m.p. being unaffected by further crystallization.

5.895 mg subs.: 0.408 ml N_2 (24°, 746 mm). 4.900 mg subs.: 0.338 ml N_2 (22°, 744 mm). Found %: N 7.81, 7.81. $C_{25}H_{30}N_2$. Calc. %: N 7.82.

Isomerization of the diketone (XII) to the keto-enol (XIII). a) As effected by temperature. A solution of 0.5 g of the diketone (XII) in 10 ml of benzene was heated to 125° for 7 hours in an atmosphere of carbon dioxide within a sealed ampoule. The benzene was then driven off in vacuo, and the residue was dissolved in 6 ml of hot alcohol. As the solution cooled, beautifully formed white crystals of the keto-enol (XIII) settled out. The yield was 0.25 g of a product with a m.p. of 150-151°, which was unaffected by further crystallization. Isomerization was incomplete, apparently, since the color of the mother liquor was yellow.

The keto-enol (XIII) consisted of yellow needles (from alcohol) with a m.p. of 150-151°. It is much less soluble in organic solvents than the diketone, and insoluble in water or aqueous alkalies. Its alcoholic solution colors ferric chloride violet.

5.710 mg subs.: 16.700 mg CO_2; 4.665 mg H_2O. 5.650 mg subs.: 16.510 mg CO_2; 4.635 mg H_2O. 0.0730 g subs.: 5.50 ml CH_4 (15°, 760 mm) in the Tserevitinov test. Found %: C 79.8, 79.7; H 9.1, 9.2; OH 5.40. $C_{18}H_{25}O(OH)$. Calc.%: C 79.7; H 9.15; OH 5.92.

b) As effected by an alkali. 2 ml of 10% potassium hydroxide were added to a solution of 0.5 g of the diketone (XII) in 8 ml of dioxane, and the solution was agitated for 5 minutes. The yellow solution turned faintly greenish. The solution was chilled and neutralized with hydrochloric acid (1:1), the solution becoming colorless and white crystals beginning to settle out. When 3 ml of water were added and the whole shaken up, the whole solution became filled with crystals. They were filtered out, washed with water and then with alcohol, and dried in a desiccator. The yield was 0.45 g of the product (XIII), with a m.p. of 149-151°. Its mixed melting point with the keto-enol prepared in the previous experiment exhibited no depression.

c) As effected by piperidine. 3 to 4 drops of piperidine were added to a solution of 2.3 g of the diketone (XII) in 15 ml of anhydrous dioxane, and the mixture was allowed to stand for 2 hours, the yellow solution turning greenish. Then 12-15 ml of water were added, plus enough alcohol to make the emulsion disappear (5-10 ml). After some minutes had passed, the beautifully formed crystals of the keto-enol (XIII) began to settle out. Three hours later they were filtered out and washed with alcohol and ether. This yielded 2.0 g of crystals with a m.p. of 150-151°. Their mixed melting point with the keto-enol produced in the preceding experiment exhibited no depression.

Acetylation of the keto-enol (XIII). 2.1 grams of the keto-enol (XIII) were heated in 10 ml of acetic anhydride until they dissolved, the solution was allowed to cool, 2 ml of anhydrous pyridine were added, and the whole was set aside to stand overnight. The next day it was poured into 60 ml of water and the separated oil was washed repeatedly by decantation. When the oil was rubber under water it crystallized. Crystallization from 10 ml of 75% alcohol yielded 1.4 g of the acetate (XV) as large crystals with a m.p. of 64-65°.

5.574 mg subs.: 15.612 mg CO_2; 4.586 mg H_2O. 5.421 mg subs.: 15.174 mg CO_2; 4.520 mg H_2O. Found %: C 76.4, 76.4; H 9.2, 9.3. $C_{21}H_{28}O_3$. Calc. %: C 76.8; H 8.6.

Saponification with an alcoholic solution of sodium hydroxide in the cold yielded the intial keto-enol (XIII).

Hydrogenation of the keto-enol (XIII). The keto-enol (XIII) cannot be hydrogenated in the cold, whether with a Pd catalyst, an Adams Pt catalyst, or platinized charcoal in the presence of H_2PtCl_6. Nor can the keto-enol be hydrogenated with Raney's nickel in an autoclave at 80 atm of hydrogen, even at 80°, as is readily disclosed by the color reaction with ferric chloride. Only by raising the temperature to 120° can the desired result be achieved.

1.5 grams of the keto-enol (XIII) in 20 ml of alcohol were hydrogenated in a revolving autoclave at 120° and a hydrogen pressure of 90 atm for 5 hours in the presence of Raney's nickel. The solution then did not color ferric chloride. After it had been filtered and the solvent had been driven off in

vacuo, there was left behind a thick mass, which crystallized when 5 ml of petroleum ether were added, the solution chilled, and the chilled solution rubbed with a rod. The crystals were suction filtered and washed with petroleum ether. Recrystallization from methanol yielded 0.2 g of the glycol (XXIII) with a m.p. of 150-151°, which was not affected by further recrystallization.

3.945 mg subs.: 11.390 mg CO_2; 3.625 mg H_2O. 3.366 mg subs.: 9.372 mg CO_2; 3.125 mg H_2O. 0.0812 g subs.: 13.20 ml CH_4 (20°, 740 mm) in a Tserevitinov test. Found %: C 78.8, 78.9; H 10.4, 10.4; OH 11.2 $C_{19}H_{30}O_2$. Calc. %: C 78.6; H 10.4; OH 11.7.

The glycol (XXIII) does not give a color reaction with ferric chloride. Its mixed melting point with the initial keto-enol was 125-132°.

Nor could the acetate of the keto-enol (XIII) be hydrogenated with Pt, Pd, or Raney's nickel in an autoclave at 100°.

Hydrogenation of the diketone (XII). 6.0 grams of the diketone (XII) in 80 ml of anhydrous dioxane were hydrogenated with Pt by the Adams method. Hydrogenation was complete two hours later, 470 ml of hydrogen at 18° and 760 mm having been absorbed as against 500 ml called for theoretically. Then the solution was evaporated at 40-50° in vacuo to a total volume of 15 ml, 5 ml of acetone were added, and the whole was set aside to stand overnight. The precipitated finely crystalline powder of the ketol (XVI) was suction-filtered and washed with acetone and with cold alcohol. This yielded 4.3 g of a product with a m.p. of 155-159°. The mother liquor was evaporated in vacuo to a thick consistency, 5 ml of alcohol were added, and it was set aside to crystallize. The next day the crystals were suction-filtered and washed with cold alcohol. This yielded another 0.4 g of crystals with a m.p. of 150-158°. The mother liquor was evaporated in vacuo until a large quantity of crystals settled out, which were recrystallized from 5 ml of 70% alcohol. Allowing them to stand in a freezing mixture (-12°) yielded 0.6 g of the ketol (XVII) with a m.p. of 117-118°. Another 0.4 g of the ketol (XVII), with a m.p. of 114-117°, was recovered from the mother liquor.

After the ketol (XVI) had been recrystallized from acetone or alcohol, it had a melting point of 159-162°, with apparent decomposition. Its melting point was higher when heating was rapid, though the melting point was just as broad. Crystallization did not produce a sharp melting point. The ketol did not produce a color reaction with ferric chloride.

7.055 mg subs.: 20.485 mg CO_2; 6.245 mg H_2O. 7.632 mg subs.: 22.135 mg CO_2; 6.615 mg H_2O. 0.0566 g subs.: 8.70 ml CH_4 (20°, 723 mm). 0.0990 g subs.: 14.85 ml CH_4 (20°, 723 mm). Found %: C 79.2, 79.2; H 9.9, 9.7; OH 10.3, 10.6. $C_{19}H_{27}O(OH)$. Calc. %: C 79.1; H 9.8; OH 5.90.

The dinitrophenylhydrazone was produced by boiling alcoholic solutions of the components with a small amount of hydrochloric acid for three hours. The yield was about 20%. Ruby-red crystals (from alcohol) with a m.p. of 193-194°.

3.840 mg subs.: 0.404 ml N_2 (24°, 748 mm). 4.025 mg subs.: 0.421 ml N_2 (24°, 746 mm). Found %: N 11.9, 11.8. $C_{25}H_{32}O_5N_4$. Calc. %: N 12.0.

After the ketol (XVII) had been recrystallized from 70% alcohol, its m.p. was 117-118°. It did not exhibit a color reaction with ferric chloride.

10.52 mg subs.: 30.65 mg CO_2; 9.43 mg H_2O. 11.37 mg subs.: 32.89 mg CO_2; 10.20 mg H_2O. 0.0972 g subs.: 14.75 ml CH_4 (20°, 740 mm). 0.1176 g subs.: 17.80 ml CH_4 (20°, 740 mm) in the Tserevitinov test. Found %: C 79.5, 78.9; H 10.0, 10.0; OH 10.45, 10.45. $C_{19}H_{27}O(OH)$. Calc. %: C 79.1; H 9.8; OH 5.90.

The dinitrophenylhydrazone, prepared as described above, had a m.p. of 187-191°, and its mixed melting point with the dinitrophenylhydrazone of the ketol (XVI) exhibited no depression.

Isomerization of the ketol (XVII). a) 100 milligrams of the ketol (XVII) with a m.p. of 115-117° were dissolved in 2 ml of methanol, and 0.3 ml of concentrated hydrochloric acid was added. The mixture was heated to 60° for two minutes. As it cooled, well-formed crystals (40 mg) with a m.p. of 152-156° settled out. Their mixed melting point with the ketol (XVI) was 153-157°.

b) 120 milligrams of the ketol (XVII) were dissolved in 3 ml of methanol, 0.5 ml of a 50% solution of sodium methylate was added, and the whole was allowed to stand overnight in a current of nitrogen. The next day it was neutralized, by the litmus paper test, with 10% hydrochloric acid, and 1.5 ml of water were added. After the mixture had stood for two hours, the finely crystalline precipitate was suction-filtered and washed with water and with alcohol. Because of its low melting point (145-152°) it was crystallized from acetone. This yielded 80 mg of crystals with a m.p. of 155-159°, which exhibited no depression when mixed with the ketol (XVI).

Treating the acetate (XIX) with hydrochloric acid in methanol did not yield the expected isomeric acetate (XVIII), the bulk of the product consisting of the original acetate plus a small quantity of the ketol (XVI), produced by saponification of the acetate followed by isomerization in the acid medium. Sodium methylate also saponifies the acetate (XIX), followed by isomerization of the ketol (XVII) to the ketol (XVI).

Acetylation of the ketol (XVI) was carried out as for the keto-enol (XIII).

4.3 grams of the ketol yielded 3.7 g of the acetate (XVIII) as large crystals with a m.p. of 124-124.5°. It does not color ferric chloride.

11.05 mg subs.: 31.02 mg CO_2; 9.12 mg H_2O. 0.1288 g subs.: 9.25 ml CH_4 (20°, 740 mm) in the Tserevitinov test. Found %: C 76.6; H 9.2; OH 5.0. $C_{21}H_{28}O_2(OH)$. Calc. %: C 76.3; H 9.2; OH 5.15.

Saponification of the acetate (XVIII). 2.5 grams of the acetate (XVIII) were dissolved in 30 ml of warm alcohol, 3 ml of 40% potassium hydroxide were added, and the mixture was allowed to stand for three hours, after which it was neutralized and set aside to stand overnight. The next day the precipitate was suction-filtered and washed with alcohol, with water, and again with alcohol. This yielded 0.45 g of a crystalline white powder with a m.p. of 157-161°, whose mixed melting point with the initial ketol (XVI) exhibited no depression. The mother liquor yielded 0.5 g of a substance with a melting point of approximately 200°, which was soluble in alkalies and was the dicarboxylic acid (XXI).

Purifying the alkaline solution by reprecipitation and recrystallizing the precipitate from acetic acid yielded white crystals with a m.p. of 199-201° (corr.), though softening set in at 195-196°.

8.18 mg subs.: 21.16 mg CO_2; 6.31 mg H_2O. 8.07 mg subs.: 20.99 mg CO_2; 6.32 mg H_2O. 40.0 mg subs.: 2.67 ml 0.1 N KOH. Found %: C 70.6, 71.0; H 8.7, 8.8. M 304. $C_{19}H_{28}O_4$. Calc. %: C 71.2; H 8.75. M 320.

Acetylation of the ketol (XVII). 0.5 gram of the ketol (XVII) was acetylated by the same procedure employed for the keto-enol (XIII). When the acetate, which settled out as an oil, was triturated with aqueous methanol, it quickly crystallized. Crystallization from methanol yielded 0.3 g of the acetate (XIX) with a m.p. of 108-109°. It did not color ferric chloride.

5.574 mg subs.: 15.612 mg CO_2; 4.586 mg H_2O. 5.421 mg subs.: 15.174 mg CO_2; 4.520 mg H_2O. 0.1050 g subs.: 7.50 ml CH_4 (20°, 740 mm) in the Tserevitinov test. Found %: C 76.3, 76.4; H 9.2, 9.3; OH 5.0. $C_{21}H_{28}O_2(OH)$. Calc. %: C 76.3; H 9.2; OH 5.15.

Oxidation of the ketol (XVI) to the dicarboxylic acid (XXI). 3.6 grams of the ketol (XVI) were dissolved in 100 ml of hot alcohol, 10 ml of 20% potassium hydroxide were added, and the whole was set aside to stand overnight. The next day air was blown through the solution for 4 hours. 50 ml of water were added, and then the transparent, light-green solution was evaporated in vacuo to 60 ml. The 0.3 g of yellow precipitate was filtered out, and the filtrate extracted three times with ether (using a total of 100 ml). The ether extract yielded 0.2 g of the initial ketol (XVI). The aqueous solution was chilled and then acidified with hydrochloric acid until its reaction with Congo red was acid. The resultant white flocs conglomerated at first into a soft cake, but turned into a solid powder upon standing and rubbing. The powder was suction-filtered, washed with water, and air-dried, yielding 3.1 g of the acid (XXI) as minute crystals with a m.p. of 200-203° (corr.). The mother liquor yielded, in addition to the acid, 0.4 g of the acid's anhydride (XXII) as prisms with a m.p. of 99-100°.

Conversion of the dicarboxylic acid (XXI) into its anhydride (XXII). 0.5 grams of the acid (XXI) was heated in 3-4 ml of acetic anhydride on a water bath for 10 minutes. The acetic anhydride was driven off in vacuo on a water bath, 2 ml of ether were added to the residue, and the whole was chilled. This yielded 0.15 g of crystals of the anhydride (XXII) with a m.p. of 96-98°. The anhydride's melting point rose to 99-100° after crystallization from ether.

3.490 mg subs.: 9.713 mg CO_2; 2.770 mg H_2O. 4.680 mg subs.: 13.044 mg CO_2; 3.699 mg H_2O. Found %: C 76.0, 76.0; H 8.9, 8.8. $C_{19}H_{26}O_3$. Calc. %: C 75.5; H 8.7.

When the anhydride was boiled with 0.1 N KOH, it was completely saponified within three hours.

110.5 mg subs.: 7.72 ml 0.1 N KOH. M found 296; calculated 302.

Oxidation of the ketol (XVII) to the dicarboxylic acid (XXI). 0.3 grams of the ketol (XVII) with a m.p. of 116-117° was dissolved in 3 ml of alcohol, 1 ml of 20% potassium hydroxide was added, and the mixture was allowed to stand for two days. Then it was filtered, the filtrate being evaporated in vacuo, diluted with 10 ml of water, and extracted three times with ether (using a total of 30 ml). The aqueous solution was acidulated in the cold until its reaction with Congo red was acid. White flocs settled out, which soon conglomerated into a lump. When the lump was rubbed it turned into a white powder (0.2 g) with a m.p. of 198-200°. Crystallization from 5 ml of 90% acetic acid yielded 0.1 g of the dicarboxylic acid (XXI) with a m.p. of 199.5-201.5°. Its mixed melting point with the dicarboxylic acid secured in the previous test exhibited no depression.

Reduction of α-tetralone to the pinacol (XXIV). A mixture of 10 g of α-tetralone (b.p. 140-143°/21 mm), 7.5 g of absolute alcohol, 50 ml of absolute benzene, 4 g of metallic aluminum in granular form, and 0.3 g of mercuric

chloride were heated to 60-65° for 4 hours and to 80° for 1.5 hours. The reaction set in 5 to 10 minutes after heating was begun, the dark-gray reaction mass turning very thick toward the end of the reaction. 30 ml of absolute alcohol was then added, and heating at 80° was continued for another 4 hours. The reaction mass was chilled and then decomposed with 300 ml of 8% hydrochloric acid, the upper layer being removed, and the aqueous layer extracted twice with benzene. The benzene was driven off at a low vacuum, part of the residue crystallizing. The crystals were suction-filtered and washed with cold benzene. This yielded 4.8 g of the pinacol (XXIV) with a m.p. of 175-178°. Double recrystallization from hot benzene yielded a product with the constant melting point of 178-179°.

4.520 mg subs.: 13.579 mg CO_2; 3.080 mg H_2O. 4.582 mg subs.: 13.775 mg substance; 3.140 mg H_2O. Found %: C 82.0, 82.0; H 7.6, 7.7. $C_{20}H_{22}O_2$. Calc. %: C 81.6; H 7.5.

Dehydration of the pinacol (XXIV) to 3,4,3',4'-tetrahydro-1,1'-binaphthyl (XXV). 2 grams of the pinacol (XXIV) were refluxed for two hours in 10 ml of glacial acetic acid. Upon cooling 1.53 g of crystals of the hydrocarbon (XXV) with a m.p. of 138-139° settled out.

5.530 mg subs.: 18.805 mg CO_2; 3.435 mg H_2O. 4.470 mg subs.: 15.245 mg CO_2; 2.855 mg H_2O. Found %: C 92.8, 92.9; H 6.95, 6.97. $C_{20}H_{16}$. Calc. %: C 93.03; H 6.97.

Condensation of 3,4,3',4'-tetrahydro-1,1'-binaphthyl (XXV) with maleic anhydride. A solution of 1 g of maleic anhydride and 1 g of the hydrocarbon (XXV) in 8 ml of xylene was refluxed for three hours. As it cooled, 1.0 g of crystals of the addition product (XXX) was precipitated. Their melting point was 234-237° after crystallization from a mixture of benzene and acetic anhydride.

4.870 mg subs.: 14.415 mg CO_2; 2.485 mg H_2O. 5.190 mg subs.: 15.400 mg CO_2; 2.615 mg H_2O. Found %: C 80.8, 81.0; H 5.7, 5.7. $C_{24}H_{20}O_3$. Calc. %: C 80.9; H 5.7.

Condensation of 3,4,3',4'-tetrahydro-1,1'-binaphthyl (XXV) with 1,3-dimethyl-Δ'-cyclopenten-5-one (IV). a) 0.5 gram of the hydrocarbon (XXV), 4 g of the cyclopentenone (IV), and 0.01 g of pyrolgallol were heated together to 195-200° for 38 hours in an atmosphere of nitrogen within a sealed ampoule. The residue crystallized after the excess of the ketone had been driven off in vacuo. We recovered 0.32 g of the initial hydrocarbon.

b) 0.5 gram of the hydrocarbon (XXV) was heated for 3 hours to 345-350° with 3 g of the cyclopentenone (IV) and 0.01 g of pyrogallol, the conditions being the same as in the preceding experiment. The tarry mass yielded 0.2 g of the initial hydrocarbon.

c) 1.0 gram of the hydrocarbon (XXV) was heated for 6 hours to 195-220° with 7 g of the cyclopentenone (IV) and 0.1 g of chloroacetic acid, the conditions being the same as in the preceding experiment. After the ketone had been driven off in vacuo there was left an uncrystallizable, black, tarry mass. The same negative results were obtained when sulfur dioxide was added to the reaction mixture.

Condensation of 3,4,3',4'-tetrahydro-1,1'-binaphthyl (XXV) with 1,3-dimethyl-Δ'-cyclopentene-4,5-dione (V). 0.4 gram of the hydrocarbon (XXV) and 0.18 g of the dione (V) were placed in 6 ml of benzene and heated for 6 hours to 120° in a nitrogen atmosphere within a sealed ampoule. This yielded 0.33 g

of the initial hydrocarbon. Even raising the temperature to 200° failed to yield positive results, about 70% of the initial hydrocarbon being recovered.

Reduction of 6-methoxytetralone-1. A mixture of 40 g of 6-methoxytetralone, with a m.p. of 77-78°, 300 ml of absolute alcohol, 170 ml of absolute benzene, 16 g of metallic aluminum in granular form, and 1.2 g of mercuric chloride was heated to 40-45° for 3.5 hours. The reaction set in at 25-30°, the mass thickening considerably toward the end of the reaction. Then 150 ml of absolute alcohol were added, and heating was continued for another 8 hours at 45-50°. The reaction mass was then chilled and decomposed with 8% hydrochloric acid, the upper layer being removed, and the aqueous layer twice extracted with benzene. The benzene was driven off at a low vacuum. The dark-brown mass was diluted with twice its volume of ether, a crystalline precipitate of 12.5 g, with a m.p. of 125-132° being thrown down. Crystallization from dioxane yielded 5.0 g of a product with a m.p. of 140-145°.

13.54 mg substance: 35.85 mg CO_2; 9.52 mg H_2O. 9.73 mg substance: 25.80 mg CO_2; 6.71 mg H_2O. 0.0557 g substance: 1.60 ml CH_4 (18°, 740 mm). 0.0378 g substance: 1.20 ml CH_4 (18°, 740 mm) in the Tserevitinov test. Found %: C 72.1, 72.4; H 7.85, 7.7; OH 2.03, 2.22. $C_{22}H_{24}O_2(OH)_2$. Calculated %: C 74.6; H 7.3; OH 9.65.

When 1.0 g of the substance was boiled for 5 minutes in 10 ml of acetic acid and the acid then driven off in vacuo at 60°, we secured a viscous liquid. A small amount of crystals with a m.p. of 60-70° settled out when the liquid stood for a day. The compound (XXVIII) should have a melting point of 148° according to the literature [12].

SUMMARY

1. Di-Δ'-cyclohexenyl (I) has been condensed with the following cyclic ketones: Δ'-cyclohenxenone (II); 1-methyl-Δ'-cyclohexen-6-one (III); and 1,3-dimethyl-Δ'-cyclopenten-5-one (IV); and the respective tetracyclic ketones (VI, IX, X, and XI) have been produced with yields ranging up to 30%. Condensing di-Δ'-cyclohexenyl (I) with 1,3-dimethyl-Δ'-cyclopenten-5-one (IV) yielded the two theoretically possible stereo isomers, (X) and (XI).

2. Condensing the dicyclohexenyl (I) with 1,3-dimethyl-Δ'-cyclopenten-4,5-dione (V) at 100° has yielded the tetracyclic diketone (XII), while condensation at 120° yielded the tetracyclic keto-enol (XIII). The diketone (XII) has been smoothly isomerized to the keto-enol (XIII) under the action of temperature (120°), as well as of organic and inorganic bases.

3. It has been shown that hydrogenating the diketone (XII) yields a mixture of isomeric ketols, (XVI and XVII), which are readily oxidized by atmospheric oxygen in an alkaline medium to the same tricyclic dicarboxylic acid (XXI). When the ketol (XVII) is reacted with hydrochloric acid or sodium methylate, it is isomerized to the ketol (XVI). The keto-enol (XIII) is hydrogenated only at 110° under pressure, the ketonic group being hydrogenated as well as the double bond in the five-membered ring. In no instance of hydrogenation is a double bond in a six-membered ring of the condensed system affected.

4. 3,4,3', 4'-Tetrahydro-1, 1'-binaphthyl (XXV) has been condensed with maleic anhydride, yielding the normal diene-synthesis product (XXX). The hydrocarbon (XXV) does not condense with 1,3-dimethyl-Δ'-cyclopenten-5-one (IV) or 1,3-dimethyl-Δ'-cyclopentene-4,5-dione (V), even at 200-230°.

5. The reduction of the following ketones to pinacols by using aluminum and magnesium has been tested: 6-methoxytetralone-1; α-tetralone; and 9-methyl-Δ^6-octalone-1. The first of these ketones yields a mixture of products that contains

very little of a pinacol, while the other two cannot be reduced to the respective pinacols at all.

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ISOMERIZATION OF THE DISACCHARIDES

II. ISOMERIZATION OF GALACTOSIDO-3-GLUCOSE

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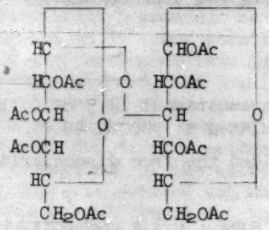
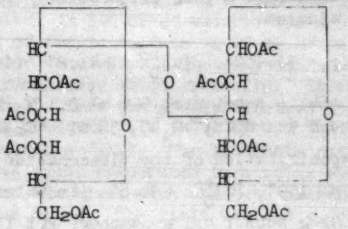
In a previous report, one of the present authors has shown [1] that acetylated glucosido-3-glucose dissolved in chloroform is converted by askanite into acetylated glucosido-3-mannose, which is epimeric with the original disaccharide.

The present paper describes similar experiments performed on galactosido-3-glucose. When galactosido-3-glucose [2] is reacted with acetic anhydride, it is first converted into an acetylated disaccharide (I). Agitating a chloroform solution of the acetylated disaccharide with askanite yields a new acetylated disaccharide, owing to a rearrangement that occurs at the second carbon atom in the reducing portion of the disaccharide. The resultant crystals were first refined by recrystallizing them from ethyl alcohol, and then chromatographically on alumina. It was found that these crystals were the octaacetate of galactosido-3-mannose (II). Saponification of (II) yielded galactosido-3-mannose (III).



(I)



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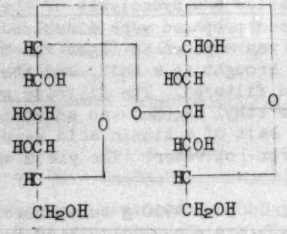
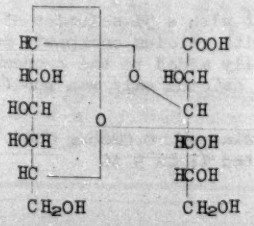
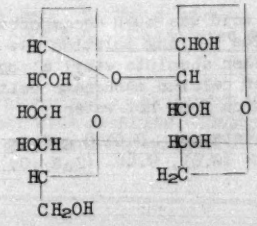


(III)

Oxidizing the disaccharide with bromine water yielded galactosido-3-mannonic acid (IV), which yielded galactose and mannonic acid upon hydrolysis.



(IV)



(V)

Oxidation of the calcium salt of galactosido-3-d-mannonic acid with hydrogen peroxide in the presence of iron salts yielded galactosido-2-d-arabinose (V). Galactosido-2-d-arabinose yields nothing but a hydrazone, which indicates the position of the oxygen bridge in this disaccharide (1,2) and in the resultant galactosido-3-mannose (1,3).

Hence, the position of the oxygen bridge in galactosido-3-glucose does not change during isomerization.

EXPERIMENTAL

1. Isomerization of acetylated galactosido-3-glucose. 100 grams of anhydrous askanite was added to a solution of 25.8 g of the octaacetate of galactosido-3-glucose (m.p. 141-143°) in 350 ml of anhydrous chloroform, placed in a round-bottomed flask fitted with a reflux condenser. The mixture was agitated in the cold for 10 days, the flask contents being heated to 70° toward the end of this time. The askanite was filtered out of the slightly colored solution, which was evaporated to a thick syrup. The residual mass crystallized during the course of a few hours. The crystals, recrystallized from ethyl alcohol, proved to be heterogeneous when examined microscopically. The substance was apparently contaminated with the original product. The substance was then recrystallized repeatedly from ethyl alcohol to secure a pure preparation. Further refining was done chromatographically on alumina.

M.p. 151-152°, $[\alpha]_D^{20}$ +41.2° (in chloroform).

0.0841 g substance: 9.6 ml 0.1 N. NaOH 0.1101 g substance: 12.5 ml 0.1N NaOH. Found %: $COCH_3$ 49.45, 50.01. $C_{28}H_{38}O_{19}$. Calculated %: $COCH_3$ 49.25.

Saponification of the disaccharide acetate yielded the free disaccharide.

M.p. 159°, $[\alpha]_D^{20}$ +34.8° (in water)

0.01 g subs.; 0.1 g camphor: Δt 11.5°; 0.01 g subs.; 0.1 g camphor: Δt 11.3°. Found: M 347, 354. $C_{12}H_{22}O_{11}$. Calculated: M 342.

2. Oxidation of the disaccharide and hydrolysis of the resultant acid. 15.4 grams of the new disaccharide we had prepared were dissolved in 300 ml of bromine water, and the resulting solution was exposed to light for 5 days with frequent agitation. Then the solution was brought to a boil, and the boiling solution neutralized with calcium chloride and filtered. The filtrate was concentrated to a small volume, after which absolute ethyl alcohol was added to it gradually. The precipitated flocs of the calcium salt of a bionic acid were filtered out and refined by recrystallizing them from hot water. The yield was 13.1 g, or 78% of the theoretical.

0.2510 g substance: 0.0214 g CaO; 0.4900 g substance: 0.0378 g CaO. Found %. Ca 6.10, 5.51. $(C_{12}H_{21}O_{12})_2Ca$. Calculated %: Ca 5.30

Precipitating the calcium from 6 g of the calcium salt with the computed quantity of oxalic acid, followed by evaporation of the filtered solution, yielded the bionic acid as a syrup.

The bionic acid was then decomposed by boiling it with a 5% solution of sulfuric acid. The boiling solution was neutralized with calcium carbonate and then filtered. When absolute ethyl alcohol was gradually added to the condensed solution, flocs of calcium mannonate settled out. The calcium salt was purified by recrystallization from hot water.

0.1189 g substance: 0.0168 g CaO; 0.2001 g substance: 0.0268 g CaO. Found %: Ca 10.01, 9.60. $(C_6H_{11}O_7)_2Ca$. Calculated %: Ca 9.30

Decomposing the calcium mannonate with the computed quantity of oxalic acid, followed by evaporation of the filtered solution, yielded crystals of the lactone of mannonic acid with a m.p. of 149-150°, $[\alpha]_D^{20}$ +50.8° (in water), which agrees with the figures given in the literature [3]. The mixed melting point with a known sample of the mannonic acid lactone exhibited no depression.

0.1658 g subs.: 0.2892 g CO_2; 0.0808 g H_2O; 0.0995 g subs.: 0.1680 g CO_2; 0.0509 g H_2O. Found %: C 46.81, 46.96; H 5.26, 5.70. $C_6H_{10}O_6$. Calculated %: C 46.05; H 5.68.

Phenylhydrazide:: m.p. 213-214°; $[\alpha]_D^{20}$ -15.8° (in water).

0.1325 g subs.: 11.7 ml N_2 (16°, 740 mm); 0.2118 g subs.: 18.4 ml N_2 (16°, 740 mm). Found %: N 10.21, 10.01. $C_{12}H_{18}O_6N_2$. Calculated %: N 9.75

After the calcium mannonate had been filtered out, the solution was boiled with 6 ml of acetic acid and 6 g of phenylhydrazine. As the solution cooled, yellow crystals settled out. They were filtered out and purified by recrystallization from ethyl alcohol. The melting point of the pure product was 194-196°. Their mixed melting point with a known sample of galactosazone exhibited no depression.

3. Oxidation of galactosido-3-mannonic acid. 5.1 grams of the calcium salt of galactosido-3-mannonic acid were dissolved in 100 ml of water. The solution was heated to 70°, and solutions of 1.2 g of ferric sulfate in 20 ml of water and of 1.6 g of barium acetate in 20 ml of water were added. The reaction mixture was vigorously stirred, and 30 ml of 30% perhydrol were added gradually. Three hours later 10 more ml of the perhydrol were added. Then the precipitate was filtered out, and the solution was evaporated at reduced pressure to a thick syrup. The syrup was mixed with 300 ml of a methanol--acetone mixture (1:1). The insoluble matter was filtered out of the solution, which was again evaporated to a thick syrup. White crystals settled out when the residue was mixed with absolute methanol. The crystals were filtered out the next day and dried. The yield was 1.8 g, or 53% of the theoretical.

M.p. 143-144°, $[\alpha]_D^{20}$ +34.4° (in water)

0.1090 g subs.: 0.1691 g CO_2; 0.0693 g H_2O; 0.1218 g subs.: 0.1889 g CO_2; 0.0712 g H_2O. Found %: C 42.06, 42.40; H 6.90, 6.42. $C_{11}H_{20}O_{10}$. Calculated %: C 42.30; H 6.41.

The m.p. of the acetylated galactosido-2-d-arabinose was 139-142°, $[\alpha]_D^{20}$ +40.6° (in chloroform).

0.1261 g subs.: 13.9 ml 0.1 N NaOH; 0.1656 g subs.: 19.1 ml 0.1 N NaOH. Found %: $COCH_3$ 50.15, 49.89. $C_{25}H_{34}O_{17}$. Calculated %: $COCH_3$ 49.60.

When the galactosido-2-d-arabinose was boiled with phenylhydrazine and acetic acid, and the solution then evaporated to small volume, crystals of the hydrazone of galactosido-2-d-arabinose settled out; they were refined by recrystallization from alcohol.

M.p. 184-186°.

0.1469 g subs.: 9.4 ml N_2 (15°, 738 mm); 0.1644 g subs.: 10.2 ml N_2 (15°, 738 mm). Found %: N 7.45, 7.08. $C_{17}H_{26}N_2O_9$. Calculated %: N 6.96.

SUMMARY

1. Galactosido-3-mannose has been synthesized by agitating a chloroform solution of acetylated galactosido-3-glucose with askanite. Saponifying the acetylated galactosido-3-mannose yielded galactosido-3-mannose.

2. Oxidizing the calcium salt of galactosido-3-mannonic acid with hydrogen peroxide yielded galactosido-2-d-arabinose.

3. The galactosido-3-mannose and the galactosido-2-d-arabinose have been identified via several of their derivatives.

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THE SYNTHESIS OF DISACCHARIDES

VII. SYNTHESIS OF MANNOSIDO-2-MANNOSE

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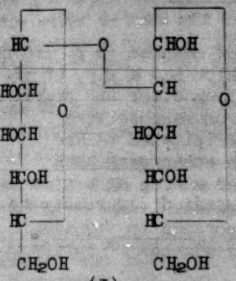
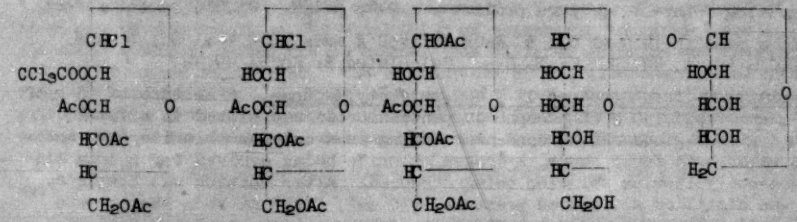
In our preceding research we synthesized the disaccharide glucosido-2-galactose [1]. The present paper describes the synthesis of mannosido-2-mannose (I).

The disaccharide has been synthesized from 2,3,4,6-tetraacetylmannose and 1,3,4,6-tetraacetylmannose. The 2,3,4,6-tetraacetylmannose was prepared by reacting acetobromomannose with silver carbonate [2]. The 1,3,4,6-tetraacetylmannose (IV) was prepared by reacting mannose pentaacetate with an excess of phosphorus pentachloride, followed by hydrolysis of the resulting monochloro-2-(trichloroacetyl)-3,4,6-triacetylmannose (II) and acetylation of the 1-chloro-3,4,6-triacetylmannose (III).



(I)

The 2,3,4,6-tetraacetylmannose was condensed with the 1,3,4,6-tetraacetylmannose in a chloroform solution, at first in the presence of zinc chloride and stannic chloride and then with phosphoric anhydride present. Saponification of the resultant disaccharide octaacetate yielded the disaccharide itself with the empirical formula of $C_{12}H_{22}O_{11}$. When reacted with phenylhydrazine, the disaccharide produces nothing but a hydrazone.



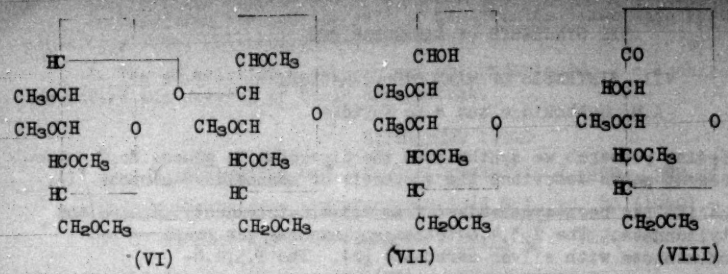
(II) (III) (IV) (V)

The bionic acid produced by oxidizing the disaccharide with bromine water was oxidized with hydrogen peroxide to determine the disaccharide's structure. The resultant mannosido-2-arabinoside (V) did not reduce Fehling's solution nor did it react with phenylhydrazine.

The disaccharide was methylated, hydrolyzed, and oxidized to settle the question of the position of the oxygen bridges within the disaccharide's monoses. The properties of the tetramethylmannose (VII) and of the lactone of trimethylmannonic acid (VIII) secured from the methylated mannosido-2-mannose (VI), indicated that they were 2,3,4,6-tetramethyl-d-mannopyranose and the δ-lactone of 2,3,6-trimethylmannonic acid, respectively.

Thus, the oxygen bridges are located in the 1,5 position in both of the monoses that make up the disaccharide.

Hence, the disaccharide we have synthesized has the structure of (1,5)-mannosido-2-(1,5)-mannose (I).



(VI) (VII) (VIII)

EXPERIMENTAL

1. 2,3,4,6-Tetraacetylmannose. The beta pentaacetate of mannose (m.p. 120-121° $[\alpha]_D^{20}$ -25° in chloroform) yielded 1-bromotetraacetylmannose, which had a m.p. of 52-53° after it had been precipitated from chloroform with petroleum ether and proved to be fairly pure product upon analysis. 20 grams of the acetobromomannose were dissolved in 200 ml of absolute ether, and 10 g of freshly precipitated silver carbonate that had been dried and washed with alcohol and with ether were then added to the resulting solution. 1.5 grams of water were added a drop at a time from a small pipet to the resultant mixture, which was then agitated vigorously for 2 hours. The solution was filtered, desiccated, and then evaporated to dryness. The resultant tetraacetylmannose was recrystallized from ethyl alcohol to purify it. The yield was 13.1 g, or 72% of the theoretical.

The melting point of the pure product was 94°, $[\alpha]_D^{20}$ +25.5° (in chloroform).

0.1265 g subs.: 14.9 ml 0.1 N NaOH, 0.1452 g subs.: 16.4 ml 0.1 N NaOH. Found %: $COCH_3$ 49.71, 49.49. $C_{14}H_{20}O_{10}$. Calculated %: $COCH_3$ 49.42.

2. 1-Chloro-2-(trichloroacetyl)-3,4,6-triacetylmannose. A mixture of 75 g of pentaacetylmannose and 130 g of phosphorus pentachloride was placed in a flask fitted with a ground-glass reflux condenser ending in a calcium chloride tube and heated on a water bath for 3 hours, hydrogen chloride being evolved for a long time and a homogeneous yellowish solution being produced. After heating was complete, the liquid was distilled at reduced pressure (10 mm), first at room temperature and then at 100°. The oily product left in the flask was dissolved in 10 ml of amyl alcohol, a precipitate settling out as the alcohol cooled; it was extracted with ether.

Desiccating the extract and evaporating the ether yielded crystals of 1-chloro-2-(trichloroacetyl)-3,4,6-triacetylmannose. The pure product had a m.p. of 134-136°; $[\alpha]_D^{20}$ +11.7° (in benzene). The yield was 54.8 g, or 56% of the theoretical.

1-Chloro-2-(trichloroacetyl)-3,4,6-triacetylmannose is freely soluble in benzene, ethyl acetate, chloroform, glacial acetic acid, methanol, and ethyl alcohol. It reduces Fehling's solution and precipitates silver chloride from silver nitrate.

0.0748 g subs.: 0.0906 g AgCl. 0.1449 g subs.: 0.1765 g AgCl. Found %: Cl 29.89, 30.45. $C_{14}H_{18}O_8Cl_4$. Calculated %: Cl 30.02.

3. 1-Chloro-3,4,6-triacetylmannose. 300 ml of absolute ether saturated with anhydrous ammonia at 0° were added to 50 g of 1-chloro-2-(trichloroacetyl)-3,4,6-triacetylmannose. After the mixture had been agitated for 5 minutes, all the 1-chloro-2-(trichloroacetyl)-3,4,6-triacetylmannose dissolved. Some hours later crystals of the ammonium salt formed; the mixture was deeply chilled and the crystals were filtered out. Then the ether solution was evaporated to dryness, the substance being extracted from the dry residue with ethyl acetate. The ethyl

acetate was evaporated, and the 1-chloro-3,4,6-triacetylmannose was recrystallized from ethyl alcohol. The pure product had a m.p. of 151-152°; $[\alpha]_D^{20}$ +17.1° (in ethyl acetate). The yield was 32.4 g, or 88% of the theoretical.

1-Chloro-3,4,6-triacetylmannose is soluble in ether, benzene, chloroform, acetone, and ethyl alcohol. The solution reduces boiling Fehling's solution and precipitates silver chloride with fused silver nitrate.

0.1501 g subs.: 0.0612 g AgCl. 0.2043 g subs.: 0.0809 g AgCl.
Found %: Cl 11.21; 11.01. $C_{12}H_{17}O_8Cl$. Calculated %: Cl 10.94.

4. 1,3,4,6-Tetraacetylmannose. 30.1 grams of 1-chloro-3,4,6-triacetylmannose were dissolved in 300 ml of absolute ether, 25.6 g of anhydrous silver acetate were added, and the mixture was agitated for 2 hours in the cold (until test samples gave a negative test for halogen in the solution). The solution was filtered, and the ether driven off in vacuo, yielding white crystals of 1,3,4,6-tetraacetylmannose with a m.p. of 131°. The substance was purified by recrystallizing it from ethyl alcohol. The substance is freely soluble in chloroform, ether, methanol, ethyl alcohol, and pyridine, and less so in water, benzene, and ligroin. The yield was 28.8 g, or 86% of the theoretical. The substance was dried in a vacuum desiccator over phosphoric anhydride for analysis.

0.1989 g subs.: 0.3513 g CO_2; 0.1062 g H_2O. 0.2159 g subs.: 24.8 ml 0.1 N NaOH. 0.3101 g subs.: 35.6 ml 0.1 N NaOH. Found %: C 48.01; H 5.89; $COCH_3$ 48.81, 49.17. $C_{14}H_{20}O_{10}$. Calculated %: C 48.28; H 5.74; $COCH_3$ 49.42.

5. Octaacetylmannosido-2-mannose. A mixture of 26.8 g of 2,3,4,6-tetraacetylmannose and 26.8 g of 1,3,4,6-tetraacetylmannose was dissolved in 400 ml of anhydrous chloroform. Then 40 g of fused zinc chloride and 4 g of stannic chloride were added to the solution, and the whole was agitated for 5 hours. The precipitate was filtered out of the solution, to which 30 g of phosphoric anhydride were added, and the whole again agitated for 10 hours. The filtered solution was evaporated at reduced pressure to dryness. The octaacetate of the disaccharide was extracted from the residue with anhydrous ether and with ethyl acetate. The combined extracts were desiccated, after which they yielded crystals of the disaccharide's octaacetate. The substance was purified by recrystallizing it from ethyl alcohol.

The yield was 42.10 g, or 81% of the theoretical. The m.p. of the pure product was 153°, $[\alpha]_D^{20}$ +19.2° (in ethyl alcohol).

0.1081 g subs.: 0.1964 g CO_2; 0.0585 g H_2O. 0.1702 g subs.: 0.2609 g CO_2: 0.0830 g H_2O. 0.1872 g subs.: 21.8 ml 0.1 N NaOH. 0.2521 g subs.: 29.4 ml 0.1 N NaOH. Found %: C 49.25, 49.01; H 5.94, 5.39; $COCH_3$ 50.41, 50.17. $C_{28}H_{38}O_{19}$. Calculated %: C 49.37; H 5.61 $COCH_3$ 50.75.

6. (1,5)-Mannosido-2-(1,5)-mannose. 36 g of the octaacetate of the disaccharide were dissolved in 150 ml of anhydrous chloroform, the resultant solution was cooled to 10 deg, and 0.9 g of sodium in 200 ml of anhydrous methanol was added. The mixture was chilled and shaken frequently for 50 minutes, a syrupy mass gradually settling out of the solution. Then 100 ml of chilled water were added to the reaction mixture, and the latter was shaken vigorously. The liquid was carefully neutralized with dilute acetic acid, and the water-alcohol layer was separated from the chloroform and evaporated in vacuo to dryness. The residue was mixed with a mixture of 300 ml of absolute methanol and 200 ml of acetone. The solution was allowed to stand for 15 minutes and then it was filtered and evaporated to the consistency of a syrup. The syrup was dissolved in 15 ml of water, the resulting solution being mixed with 30 ml of glacial acetic acid and set aside to stand overnight, the disaccharide gradually crystallizing out. The yield was 12.6 g, or 81% of the theoretical. The m.p. of the pure product was 141-143° $[\alpha]_D^{20}$ +24.5° (in water).

0.1430 g substance: 0.2249 g CO_2; 0.0794 g H_2O. 0.1722 g substance: 0.2678 g CO_2; 0.1283 g H_2O. Found %: C 42.51, 42.25; H 6.27, 6.09. $C_{12}H_{22}O_{11}$. Calculated %: C 42.08; H 6.48.

7. Oxidation of (1,5)-mannosido-2-(1,5)-mannose. 8.9 grams of (1,5)-mannosido-2-(1,5)-mannose were dissolved in 400 ml of bromine water, and the resulting mixture was exposed to the light for 3 days, during which time it was agitated vigorously. Then the excess bromine was driven off by heating, and the solution was neutralized with calcium chloride. The solution was filtered, and a solution of silver nitrate was added a drop at a time, producing an insoluble silver salt of hydrobromic acid and a soluble bionate.

The silver was eliminated from the filtered solution with hydrogen sulfide. The silver sulfide was filtered out of the solution, which was then evaporated in vacuo to small volume.

The bionic acid was further refined by treating the solution with basic lead acetate. The precipitate was filtered out, suspended in water, and decomposed with hydrogen sulfide. The lead sulfide was filtered out, and the solution was evaporated to the consistency of a syrup. The substance was mixed repeatedly with hot ethyl alcohol, the alcohol being driven off in vacuum, in order to get rid of the odor of acetic acid.

The resulting bionic acid was dissolved in 100 ml of water, the solution being heated to boiling with calcium carbonate. The excess calcium carbonate was filtered out, and the solution was evaporated until crystallization occurred. The crystals were recrystallized from hot water.

0.2621 g substance: 0.0191 g CaO. 0.3349 g substance: 0.0233 g CaO. Found %: Ca 5.21, 5.02 $(C_{12}H_{21}O_{12})_2Ca$. Calculated %: Ca 5.31.

8. Oxidation of mannosido-2-mannonic acid. 7.5 grams of the calcium salt of mannosido-2-mannonic acid were dissolved in 20 ml of water, the solution was heated to 70°, and solutions of 0.7 g of barium acetate in 10 ml of water, 0.3 g of ferric sulfate in 10 ml of water, and 30 ml of 30% perhydrol were added. Then the reaction mixture was frequently agitated as it was heated to a gentle boil and then set aside to stand at room temperature. Three hours later another 10 ml of the perhydrol were added to the solution.

Then the solution was boiled for 10-15 minutes, filtered, and evaporated to dryness. The residue was mixed with 30 ml of acetic anhydride, and the solution was heated to boiling with 3 g of fused sodium acetate on a water bath for 5 hours. The excess acetic anhydride was driven off, and the acetylated product was extracted with diethyl ether. Desiccation and evaporation of the ether left behind the crystals of hepta-acetylmannosido-d-arabinose. The substance was refined by recrystallizing it from ethyl alcohol; the m.p. of the pure product was 147-149°.

0.1149 g substance: 13.9 ml 0.1 N NaOH. 0.1483 g substance: 17.1 ml 0.1 N NaOH. Found %: $COCH_3$ 49.73, 49.69. $C_{25}H_{34}O_{17}$. Calculated %: $COCH_3$ 49.60.

The deacetylated product did not react with phenylhydrazine, nor did it reduce Fehling's solution or give a silver mirror reaction.

9. Methylation of mannosido-2-mannose. Hydrolysis of the methylated disaccharide and identification of the hydrolysis products. 10.3 grams of mannosido-2-mannose were dissolved in 200 ml of water, the solution was heated to 40-60°, and dimethyl sulfate and a 25% solution of sodium hydroxide were gradually added. A total of 60 g of dimethyl sulfate was added.

The alkali was added until the reaction was weakly alkaline. Then the reaction

mixture was heated to 100°, and the reaction product was extracted with chloroform. The syrup left after the chloroform had been evaporated was remethylated, this time using 36 g of methyl iodide and 14 g of silver carbonate. The methylated mannosido-2-mannose was extracted with chloroform, the chloroform driven off, and the residue distilled in vacuo (2 mm), n_D^{20} 1.4661; $[\alpha]_D^{20}$ -13.6° (in chloroform, c = 0.5). The yield was 18.6 g, or 54% of the theoretical.

0.1109 g substance: 0.4565 g AgI. 0.1291 g substance: 0.5317 g AgI. Found %: OCH_3 55.60, 54.94. $C_{20}H_{34}O_{11}$. Calculated %: OCH_3 54.65.

16 grams of the octamethylmannosido-2-mannose were dissolved in 20 ml of chloroform, the solution being mixed with 300 ml of a 5% solution of hydrochloric acid and then boiled for 3 hours. When heating was over, the chloroform layer was separated from the aqueous one, and the reaction product extracted three more times from the latter layer with chloroform (in 50-ml batches). The combined chloroform extracts were washed with water, desiccated with calcium chloride, and evaporated to dryness. After the residue had stood for a long time, 2,3,4,6-tetramethylmannose, with a m.p. of 50-51°; $[\alpha]_D^{20}$ +27.4° (in methanol), crystallized out. The 2,3,4,6-tetramethylmannose was identified via its anilide, with a m.p. of 143-145°; $[\alpha]_D^{20}$ -8.6° (in methanol).

0.2923 g substance: 11.6 ml N_2 (16°, 730 mm). 0.3032 g substance: 10.5 ml N_2 (16°, 730 mm). Found %: N 4.60, 4.32. $C_{18}H_{25}O_5N$. Calculated %: N 4.50.

After the 2,3,4,6-tetramethylmannose had been extracted, the solution was evaporated to dryness. The residue was mixed with 300 ml of bromine water, the resulting solution being exposed to light for 3 hours with frequent shaking. Then the solution was heated to drive off the bromine and neutralized with lead carbonate. The filtrate was decomposed with hydrogen sulfide and reneutralized with calcium carbonate. As absolute ethyl alcohol was gradually added to the condensed solution, flocs of the calcium salt of 3,4,6-trimethylmannonic acid settled out. The salt was dissolved in water, the calcium precipated from the solution with the computed quantity of oxalic acid, and the solution evaporated to dryness. The residue consisted of a lactone of 3,4,6-trimethylmannonic acid, with a m.p. of 95-96°. The rapid change of the angle of rotation indicated it was the δ-lactone: $[\alpha]_D^{20}$ +166.4° → +53.7° (within 2 minutes in water). The δ-lactone of 3,4,6-trimethylmannonic acid was identified via its phenylhydrazide, with a m.p. of 139-140°.

0.2061 g substance: 15.0 ml N_2 (16°, 730 mm). 0.2216 g substance: 15.6 ml N_2 (16°, 730 mm). Found %: N 8.48, 8.01. $C_{15}H_{24}O_6N_2$. Calculated %: N 8.54.

SUMMARY

1. A new disaccharide, mannosido-2-mannose, has been synthesized.

2. Condensing 2,3,4,6-tetraacetylmannose with 1,3,4,6-tetraacetylmannose yields the octaacetate of the disaccharide.

3. Oxidizing the calcium salt of mannosido-2-mannonic acid with hydrogen peroxide yields mannosido-d-arabinose.

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THE ACTION OF HALOGEN DERIVATIVES UPON SODIUM DI-β-METHOXYETHYLPHOSPHITE

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In the preceding paper [1] we reported that the di-β-methoxyethylphosphorous and di-β-ethoxyethylphosphorous acids formed sodium salts when reacted with metallic sodium in ether. The resulting sodium di-β-methoxyethylphosphite and di-β-ethoxyethyl phosphite react with halogenated ethers as follows:

$$(ROCH_2CH_2O)_2PONa + BrCH_2OR' = (ROCH_2CH_2O)_2P(O)CH_2OR' + NaBr$$

when the reaction products are fractionated from the reaction mixture without removing the sodium bromide, the resulting alkoxyethyl ester of the alkoxymethylphosphinic acid reacts with the sodium bromide as follows:

$$(ROCH_2CH_2O)_2P(O)CH_2OR' + NaBr = ROCH_2CH_2O(NaO)P(O)CH_2OR' + ROCH_2CH_2Br.$$

This reaction of halides with esters of alkoxymethylphosphinic acids had been observed earlier [2].

In the present paper we discuss the action of the following halogen derivatives: benzyl chloride and bromide, ethyl bromide, ethylene bromide, and acetyl chloride and bromide upon sodium di-β-methoxyethylphosphite. Benzyl chloride reacts with sodium di-β-methoxyethylphosphite as follows:

$$(CH_3OCH_2CH_2O)_2PONa + ClCH_2C_6H_5 = (CH_3OCH_2CH_2O)_2P(O)CH_2C_6H_5 + NaCl.$$

When the reaction products are fractionated, the di-β-methoxyethyl ester of benzylphosphinic acid is driven off. The sodium chloride and the ester of benzylphosphinic acid formed in the reaction do not react with each other under the distillation conditions employed. The analogous reaction with benzyl bromide takes place as follows:

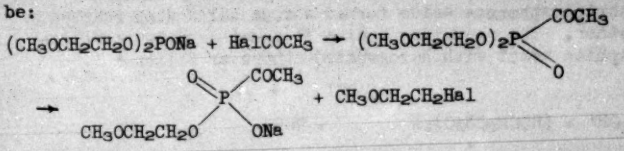
$$(CH_3OCH_2CH_2O)_2PONa + BrCH_2C_6H_5 = (CH_3OCH_2CH_2O)_2P(O)CH_2C_6H_5 + NaBr =$$

$$(CH_3OCH_2CH_2O)_2P(O)CH_2C_6H_5 + NaBr = CH_3OCH_2CH_2O(NaO)P(O)CH_2C_6H_5 + CH_3OCH_2CH_2Br.$$

The sodium salt of the β-methoxyethyl ester of benzylphosphinic acid is formed during fractionation of the reaction products. The sodium bromide formed during the reaction does react with the di-β-methoxyethyl ester of phosphinic acid under the distillation conditions which are the same as those for the sodium chloride. The reaction of ethyl bromide with sodium di-β-methoxyethylphosphite yields sodium bromide and the di-β-methoxyethyl ester of ethylphosphinic acid, which do not interact under the conditions used for fractionating the reaction products.

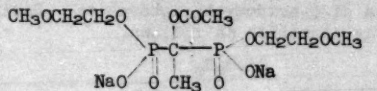
The experiments described above indicate that the formation of a salt of an ester of an alkylphosphinic acid depends, under approximately equal conditions for fractionating the reaction products, upon the nature of the halide and of the radical constituting the phosphinic acid.

Acetyl chloride and acetyl bromide react with sodium di-β-methoxyethylphosphite. The sodium chloride and sodium bromide produced in the reaction react with the resulting ester of acetylphosphinic acid, yielding the respective salt of the ester. When the reaction follows the usual course, the structure of the salt of the ester should be:

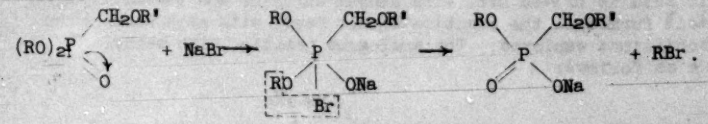


and it ought to contain a carbonyl group. M.A.Kabachnik and P.A.Rossiiskaya [3] have produced esters of acetylphosphinic acids by reacting esters of phosphorous acids with acetyl chloride. These compounds contain a carbonyl group and yield the respective hydrazones with phenylhydrazines. The salt of the ester we have secured also ought to react with phenylhydrazines, yielding hydrazones. The action of 2,4-dinitrophenylhydrazine upon our salt of the ester of acetylphosphinic acid did not yield positive results, however.

A.E.Arbuzov and M.M.Azanovskaya [4] have shown that the reaction of sodium diethylphosphite with acid halides is complicated, yielding compounds with double the molecular weight. On the basis of the negative reaction with 2,4-dinitrophenylhydrazine and in conformity with the researches of A.E.Arbuzov and M.M.Azanovskaya, the sodium salt of the β-methoxyethyl ester of acetylphosphinic acid we have synthesized must be assigned the structure of

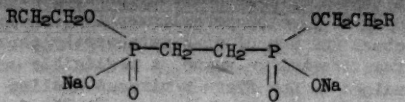


In our preceding paper we suggested a mechanism for the reaction between a sodium halide and esters of alkoxymethylphosphinic acids, involving the addition of the sodium halide at the P=O double bond, followed by splitting off an alkyl halide, as follows:



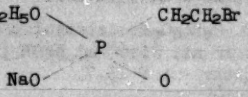
We have found that a sodium halide reacts with esters of alkylphosphinic acids only when the phosphinic acid radical contains a polar group. In the cases described, -OR' and -COR are such groups. We were, of course, interested in producing esters of alkylphosphinic acids containing other polar groups and testing the reactions of these phosphinic acids with a sodium halide. The first ester we could prepare was an ester of β-bromoethylphosphinic acid.

It was found that the reaction of a sodium dialkylphosphite with ethylene bromide varies, depending upon the order in which the reagents are added and their proportions. When equimolecular proportions of ethylene bromide and sodium di-β-methoxyethylphosphite are reacted together, and the reaction products are fractionated together with the sodium bromide produced, we get the sodium salt of the β-methoxyethyl ester of diphosphoethane:



where R = OCH_3. Reacting ethylene bromide with sodium diethylphosphite and fractionating the reaction products together with the sodium bromide yielded the ethyl ester of diphosphoethane, a solid product remaining in the distillation flask. While our research was under way, the ethyl ester of diphosphoethane has been described by Ford-Moore and Williams [5]. The constants of our preparation agreed with those given by them. Analysis of the solid product indicated that it was the sodium salt of the ethyl ester of diphosethane, with the structure given above, where R = H.

Reacting sodium diethylphosphite with an excess of ethylene bromide and then fractionating the reaction products with the sodium bromide yielded the sodium salt of the ethyl ester of β-bromoethylphosphinic acid:



It follows from the foregoing that the active polar atom of bromine in β-bromoethylphosphinic acid makes the reaction between sodium bromide and the ethyl ester of β-bromoethylphosphinic acid possible. It should be added, however, that the radicals in the ester groups also appear to affect the course of this reaction.

We have also noticed that no sodium iodide is thrown down when alkyl iodides are reacted with sodium di-β-methoxyethylphosphite, even though the ether solution be heated until ether boils.

EXPERIMENTAL

Action of benzyl chloride upon sodium di-β-methoxyethylphosphite. 3 grams of benzyl chloride were added to sodium di-β-methoxyethylphosphite, prepared from 0.55 g of metallic sodium in 30 ml of anhydrous ether and 5 g of di-β-methoxyethylphosphorous acid. The reaction products were briefly heated and then fractionated in vacuo, a small quantity of a product with a b.p. of 180-188°/10 mm; n_D^{20} 1.4708, being driven off. The product left within the flask proved to be sodium chloride, upon analysis.

The following experiment was run to identify the liquid product: 8.5 g of benzyl chloride were added to sodium di-β-methoxyethylphosphite, prepared from 1.5 g of sodium in 70 ml of ether and 15 g of di-β-methoxyethylphosphorous acid. After the mixture had been heated on a water bath, the ether layer was decanted from the sodium chloride formed. The ether was driven off, and the residue fractionated in vacuo, yielding the following fractions (at 13 mm): I 40-140°, 2.7 g, n_D^{20} 1.4960; II 140-191° 2.3 g, n_D^{20} 1.4970; III 191-197°, 11.9 g, n_D^{20} 1.4945. A fraction with a b.p. of 190-193°/11 mm was collected from Fractions II and III after two successive fractionations. The ester yield was 12 g, or 55% of the theoretical.

n_D^{20} 1.4945; d_4^{20} 1.156; MR_D 72.63. $C_{13}H_{21}O_5P$. Calculated 72.37.
0.1296 g, 0.1883 g substance: 18.6 ml 26.05 ml NaOH (T = 0.02843).
Found %: P 11.2, 10.88. $C_{13}H_{21}O_5P$. Calculated %: P 10.7.

Action of benzyl bromide upon sodium di-β-methoxyethylphosphite. 3.9 g of benzyl bromide were added to sodium di-β-methoxyethylphosphite, prepared from 0.55 g of sodium in 30 ml of ether and 5 g of di-β-methoxyethylphosphorous acid. The reaction products were fractionated in vacuo, a negligible amount of liquid being driven off. There remained in the flask a viscous hyaline mass, which solidified upon cooling. The residue weighed 5.4 g, or 80.8% of the theoretical.

0.1334 g, 0.1222 g substance: 21.0 ml, 18.2 ml NaOH (T = 0.02843). Found %: P 12.38, 11.73. $C_{10}H_{14}O_4PNa$. Calculated %: P 12.30.

Action of ethyl bromide upon sodium di-β-methoxyethylphosphite. 2.5 g of ethyl bromide were added to sodium di-β-methoxyethylphosphite, prepared from 5 g of di-β-methoxyethylphosphorous acid as in the previous experiments, and the reaction products were fractionated in vacuo together with the sodium bromide. Two successive fractionations of the distilled liquid yielded a fraction with a b.p. of 152-154°/9 mm. The yield of the ester of ethylphosphinic acid was 3.2 g, or 56.5% of the theoretical. Sodium bromide was left in the flask after the ester had been distilled off.

n_D^{20} 1.4338; d_4^{20} 1.114. MR_D 52.90. $C_8H_{19}O_5P$. Calculated 52.81.
0.1497 g, 0.1278 g substance: 25.12 ml, 21.67 ml NaOH (T = 0.02843). Found %: P 13.2, 13.3. $C_8H_{19}O_5P$. Calculated %: P 13.7.

Action of acetyl bromide upon sodium di-β-methoxethylphosphite. 2.8 g of acetyl bromide were added to sodium di-β-methoxyethylphosphite, prepared from 5 g of di-β-methoxyethylphosphorous acid as in the preceding experiments, and the reaction products were fractionated in vacuo. A fraction with a b.p. of 60-62°/10 mm was collected.

n_D^{20} 1.4320; d_4^{20} 1.382; MR_D 26.08. C_3H_7OBr. Calculated 25.5.

There remained in the flask a viscous mass, which solidified upon cooling into a hyaline mass. It weighed 4.65 g, or 93% of the theoretical.

0.1067 g, 0.1020 g substance: 21.1 ml 20.5 ml NaOH (T = 0.02843). Found %: P 14.75, 14.99. $C_{10}H_{20}O_{10}P_2Na_2$. Calculated %: P 15.20.

Action of acetyl chloride upon sodium di-β-methoxyethylphosphite. 1.8 g of acetyl chloride were added to sodium di-β-methoxyethylphosphite prepared as set forth above, and the reaction products were fractionated in vacuo. A small quantity of methyl-β-chloroethyl ether, with a b.p. of 42-46°/13 mm, n_D^{20} 1.4125, was distilled off. There remained within the flask a brown, hyaline mass that weighed 3.75 g, or 75% of the theoretical.

0.1300 g, 0.1412 g substance: 25.8 ml, 28.5 ml NaOH (T = 0.02843). Found %: P 14.91, 15.05. $C_{10}H_{20}O_{10}P_2Na_2$. Calculated %: P 15.20.

1 gram of the salt was dissolved in absolute alcohol and then heated with 1 g of 2,4-dinitrophenylhydrazine on a water bath for 5 hours. Upon cooling the unchanged crystals of the 2,4-dinitrophenylhydrazine settled out.

Action of ethylene bromide upon sodium di-β-methoxyethylphosphite. 4.5 grams (the equimolecular quantity) of ethylene bromide was added to sodium di-β-methoxyethylphosphite, prepared from 5 g of di-β-methoxyethylphosphorous acid. Sodium bromide settled out only after the reaction products had been heated for a long time on a water bath. Than the whole was fractionated in vacuo. A total of 2.1 g of the methyl-β-bromoethyl ester was distilled. The distilling flask contained a white mass, which was purified by dissolving it in absolute alcohol. The salt contained no halogen. The crude salt weighed 5.1 g, or 76% of the theoretical.

1.1388 g, 0.1258 g substance: 39.8 ml, 36.5 ml NaOH (T = 0.02181). Found %: P 17.3, 17.5. $C_8H_{18}H_8P_2Na_2$. Calculated %: P 17.7.

Action of ethylene bromide upon sodium diethylphosphite. 3.4 grams (0.5 mole) of ethylene bromide were added to sodium diethylphosphite, prepared from 5 g of diethylphosphorous acid. The sodium bromide settled out only after the mixture was heated on a water bath. Then the reaction products were fractionated in vacuo, a fraction whose physical properties and analysis corresponded to those of the tetraethyl ester of diphosphoethane [5] being isolated from the distillate. A white mass was left within the distillation flask; it was dissolved in absolute alcohol to eliminate its sodium bromide.

0.0490 g, 0.0415 g substance: 17.5 ml, 15.1 ml NaOH (T = 0.02181). Found %: P 21.5, 21.9. $C_8H_{14}O_6P_2Na_2$. Calculated %: P 21.4.

Action of sodium diethylphosphite upon ethylene bromide. A solution of sodium diethylphosphite, prepared from 0.8 g of metallic sodium and 5 g of diethylphosphorous acid, was added to an excess (16 g) of ethylene bromide. The sodium bromide settled out only after the mixture was heated on a water bath. Then the reaction products were fractionated, a white residue remaining in the flask; it was purified by dissolving it in absolute alcohol. The salt contained a halogen.

0.0600 g, 0.0930 g substance; 14.9 ml, 24.0 ml NaOH (T = 0.01848). Found %: P 12.7, 13.1. $C_4H_9O_3BrPNa$. Calculated %: P 12.9.

SUMMARY

1. A study has been made of the action of ethyl bromide, benzyl chloride and benzyl bromide upon sodium di-β-methoxyethylphosphite. Ethyl bromide and benzyl chloride both yielded esters of alkylphosphinic acids, while the benzyl bromide yielded a salt of the ester.

2. A study has been made of the action of acetyl chloride and acetyl bromide upon sodium di-β-methoxyethylphosphite, a salt of the ester being secured. The ester salt does not form the corresponding hydrazone with 2,4-dinitrophenylhydrazine.

3. A study has been made of the action of ethylene bromide upon sodium di-β-methoxyethylphosphite and diethylphosphite. This yielded the disodium salt of the diethyl ester of diphosphoethane, the disodium salt of the di-β-methoxyethyl ester of diphosphoethane, and the sodium salt of the ethyl ester of β-bromoethylphosphinic acid.

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[3] M. I. Kabachnik and P. A. Rossiiskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, 4, 369.

[4] A. E. Arbuzov and M. M. Azanovskaya, Proc. Acad. Sci. USSR 58, 1961 (1947).

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1) See Consultants Bureau English translation, p. 2239.

THE ACTION OF IODINE DERIVATIVES UPON A SODIUM DIALKYLPHOSPHITE

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The reaction of a sodium dialkylphosphite with halogen derivatives yields an ester of an alkylphosphinic acid and a sodium halide as end products of the reaction, as follows [1,2]:

$$(RO)_2PONa + R'Hal = (RO)_2P(=O)R' + NaHal$$

The completeness of the reaction is checked by the amount of sodium halide formed. As a rule, the sodium halide is precipitated in nearly the theoretical quantity in such reactions. Instances occur, however, especially when iodine derivatives are used, in which the quantity of sodium iodide thrown down is negligible. Abramov and Militskova have found that no sodium iodide is precipitated at all when sodium di-β-methoxyethylphosphite is reacted with iodine derivatives, even when the reaction products are heated in ether. A. E. Arbuzov and Kushkova [3] have described an experiment involving the action of sodium diethylphosphite upon the ethyl ester of iodomethylphosphinic acid in which only a negligible quantity of sodium iodide was thrown down, even after 2-3 hours of heating. A thick, honeylike mass that contained a halogen was left in the reaction vessel after the ether solution had been driven off.

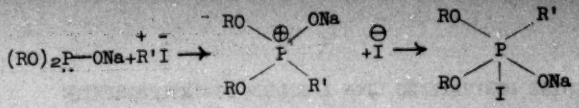
We were interested in making some observations of this singular course of the reaction between iodine derivatives and sodium salts of dialkylphosphorous acids and in endeavoring to clear up the mechanism involved in these reactions and the structure of the resultant products. Our interest herein was all the greater since these reactions are considered to be double decomposition reactions.

The reactions we have carried out between iodine derivatives and sodium diethylphosphite and di-β-methoxyethylphosphite leads us to believe that the course of these reactions resembles the action of halogen derivatives upon esters of phosphorous acid. It follows from various papers [4] that the structure of sodium dialkylphosphite must be regarded as of the enolic type, i.e., involving trivalent phosphorus. Then the reaction of iodine derivatives with a sodium dialkylphosphite may be written as occurring in two stages:

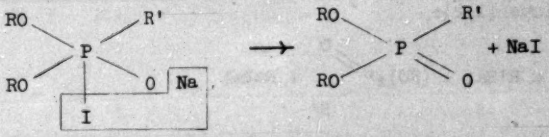
$$(RO)_2PONa + R'I = (RO)_2P(R')(I)ONa$$

$$(RO)_2P(R')(I)ONa = (RO)_2P(=O)R' + NaI$$

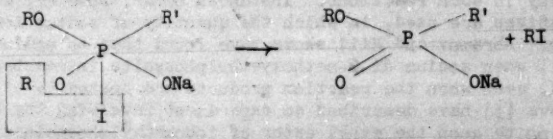
As in the esters of phosphorous acid, the reaction starts with the approach of the iodine derivative to the phosphorus atom that possesses a solitary electron pair and can share it with an electronophilic organic radical. This results in the formation of an iodine ion and a complex organic ion in which phosphorus is the central atom. The reaction concludes with the addition of the halogen atom to the atom of phosphorus.



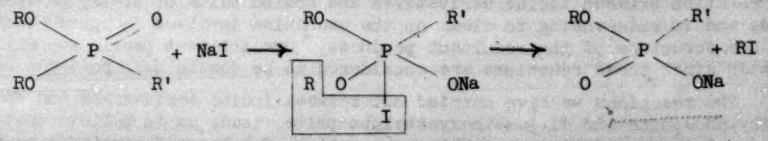
The splitting out of the sodium iodide constitutes the second stage of this process. The reaction involved in the splitting out of the sodium iodide is due to the affinity of the halogen for sodium and the stability of the resultant ester of the alkylphosphinic acid.



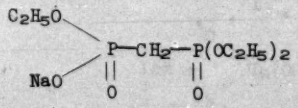
The products of the addition of the halogen derivative to the sodium dialkylphosphite may also be decomposed differently:



This decomposition procedure must be regarded as probable because the end products of our investigation, secured by heating the reaction mass to a high temperature, were salts of an ester of an alkylphosphinic acid. As we have reported earlier [5], these salts can be produced by the following reaction:



From the standpoint of the mechanism set forth above, the experiment involving the action of sodium diethylphosphite upon the ethyl ester of iodomethylphosphinic acid described by A. E. Arbuzov and Kushkova [3] may be explained by the formation of an addition product, recovered as a thick, heavy liquid that is partially soluble in ether. The porous residue left in the distillation flask after the liquid products have been distilled is probably a salt of the ester, with the composition of:



We have investigated the action of methyl, ethyl, propyl, isopropyl, and allyl iodide and of iodobenzene upon sodium diethylphosphite and di-β-methoxyethylphosphite. The experiments were carried out at room temperature under approximately equal conditions. The iodine derivative was poured into the sodium dialkylphosphite in ether, prepared from metallic sodium and the dialkylphosphorous acid [6]. Sodium iodide was thrown down when the iodine derivatives were reacted with sodium diethylphosphite. The amount of sodium

iodide precipitated varied, depending apparently upon the nature of the alkyl iodide. The results of our experiments are listed in Table 1, in which the precipitated sodium iodide is given in percent of the theoretical quantity. The next column gives the residue left after the solvent and the liquid reaction products had been driven off, recalculated in per cent of the theoretical quantity of the sodium salt of the ethyl ester of the alkylphosphinic acid.

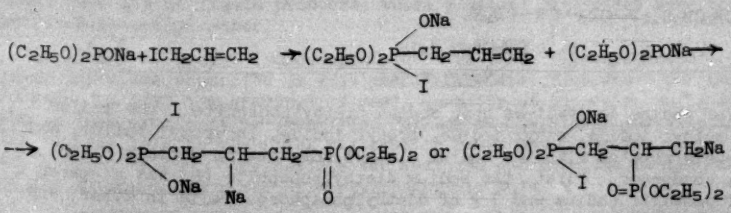
Table 1

Action of Iodine Derivatives Upon Sodium Diethylphosphite

No.	Iodine Derivative	NaI (%)	C_2H_5O, O, NaO, R' (%)	Remarks
1	Methyl iodide	73.3	21.6	An addition compound is evidently formed, the percentage being 65.3% when recalculated on that basis.
2	Ethyl iodide	66.6	30.8	
3	Propyl iodide	36.0	62.4	
4	Isopropyl iodide	10.6	124.2	
5	Iodobenzene	27.0	78.2	

As we see from Table 1, the precipitation of sodium iodide follows a regular pattern, depending upon the size of the radical. A very small amount of sodium iodide is precipitated by isopropyl iodide, which is probably due to the effect of the radical's structure. There are many references to the anomalous behavior of isopropyl [1]. When the ester was driven off from the reaction products, the isopropyl iodide was left behind as a transparent hyaline mass that showed no sign of sodium iodide. Recalculating the hyaline mass in terms of an addition product yielded 65.3%.

The behavior of allyl iodide differs from that of the iodine derivatives described above. At the start of pouring the allyl iodide into the sodium diethylphosphite, the solution becomes slightly cloudy, the cloudiness subsequently disappearing. When the reaction products are allowed to stand, two layers are formed: an upper ether layer and a lower one consisting of a thick, heavy liquid. Analysis of the lower layer indicated, in agreement with the paper by A. N. Pudovik and B. A. Arbuzov [7], that it was the product of the addition of allyl iodide to the sodium diethylphosphite, with the subsequent attachment of another molecule of sodium diethylphosphite at the double bond.

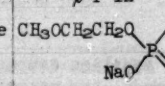
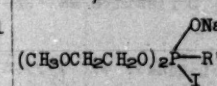


The reaction of iodine derivatives with sodium di-β-methoxyethylphosphite exhibits a state of affairs that resembles the action of allyl iodide with sodium diethylphosphite. In every instance the reaction products separated into layers, a thick, heavy layer being produced. The solvent was eliminated from the lower, viscous layer, which was then analyzed. Its percentage of

phosphorus proved to lie between the percentage in the salt of the ester of the alkylphosphinic acid and that in the addition product of allyl iodide and sodium di-β-methoxyethylphosphite. The analyses for phosphorus of the products of the action of iodine derivatives upon sodium di-β-methoxyethylphosphite are listed in Table 2.

Table 2

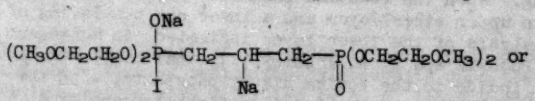
Per Cent Phosphorus Found in the Product of the Reaction Between an Iodine Derivative and Sodium Di-β-methoxyethylphosphite and Calculated for the Salt of the Ester of the Alkylphosphinic Acid and for the Addition Product

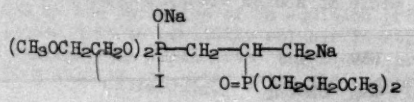
No.	Iodine Derivative	% P in 	% P Experimental	% P in 
1	Methyl iodide	17.6	11.1	8.5
2	Ethyl iodide	16.3	9.9	8.2
3	Propyl iodide	15.2	8.6	7.9
4	Isopropyl iodide	15.2	14.6	7.9
5	Iodobenzene	13.0	9.9	7.3

It was impossible to isolate the addition products in a chemically pure state from the reaction mass, which was a thick, viscous, and heavy liquid.

In several tests the viscous product was heated to high temperature in vacuo. The distillation flask contained a residue of a white, porous mass, which proved to be a salt of an ester of the respective alkylphosphinic acid upon analysis.

When one mole of allyl iodide is used to two moles of the sodium di-β-methoxyethylphosphite, we get a product that resembles the product secured in the reaction with sodium diethylphosphite, its composition being:





EXPERIMENTAL

Action of iodine derivatives upon sodium diethylphosphite. The iodine derivatives--methyl iodide, ethyl iodide, propyl iodide, isopropyl iodide, and iodobenzene--were reacted with the sodium diethylphosphite in a flask fitted with a reflux condenser. First, the sodium diethylphosphite [6] was prepared from 1.2 g of metallic sodium and 7 g of diethylphosphorous acid in ether, and then an equimolecular quantity of the iodine derivative was added at room temperature. The reaction mixture was allowed to stand until all the sodium iodide had been thrown down, after which the ether solution was decanted. The sodium iodide was freed of ether and weighed. The precipitate, dissolved in water, exhibited the qualitative reaction for sodium iodide. The decanted

ether was driven off, and the residue fractionated in vacuo, a certain amount of the ethyl ester of the respective alkylphosphinic acid being distilled in every instance. The residue was a thick, undistillable liquid, which solidified upon cooling. We assumed that this residue was the sodium salt of the ethyl ester of the respective alkylphosphinic acid. The experimental data are listed in Table 1 (vide supra).

Action of allyl iodide upon sodium diethylphosphite. 4.8 grams (0.5 mole) of allyl iodide were poured into sodium diethylphosphite, prepared from 1.3 g of metallic sodium and 8 g of diethylphosphorous acid in 80 ml of anhydrous ether. The reaction flask was water-cooled. At the start of pouring a slight cloudiness occurred, but then it disappeared. The ether solution of the reaction products separated into two layers upon standing: an upper ether layer, and a lower layer consisting of a viscous, heavy liquid. The ether layer was decanted. The ether was driven out of the lower layer by heating it in vacuo on a water bath at 35-40°. The viscous mass deliquesced in air and contained a halogen atom.

0.1364 g, 0.1196 g substance: 32.0 ml, 27.3 ml 0.5 N NaOH. 0.1364 g, 0.1196 g substance: 0.0638 g, 0.0572 g AgI. Found %: P 12.9, 12.6; I 25.3, 25.8. $C_{11}H_{25}O_6P_2Na_2I$. Calculated %: P 12.7; I 26.0.

The iodine was determined in the filtrate after the phosphorus had been determined.

Action of iodine derivatives upon sodium di-β-methoxyethylphosphite. An equimolecular quantity of the iodine derivative (3.6 g of methyl iodide, 3.9 g of ethyl iodide, 4.2 g of propyl iodide and isopropyl iodide, and 5.1 g of iodobenzene) was added to sodium di-β-methoxyethylphosphite, prepared from 0.6 g of metallic sodium and 5 g of di-β-methoxyethylphosphorous acid. At the start of pouring a slight cloudiness was observed, which quickly disappeared. Then layering occurred, the lower layer being heavy and thick. The ether solution was decanted from the lower layer. The ether was driven out of the lower layer by heating it in vacuo on a water bath at no more than 40°, and then the residue was analyzed for phosphorus. The analysis results are listed in Table 2 above. As the phosphorus analysis indicated, the thick lower layer was a mixture of the addition products of the alkyl iodide and the sodium di-β-methoxyethylphosphite plus the sodium salt of the methoxyethyl ester of the respective alkylphosphinic acid. Heating ought to yield a salt of the ester of the alkylphosphinic acid. The ether was driven out of the ether layer, and the residue was fractionated. In every run we secured a small quantity of liquid products, whose physical properties were those of methyl-β-iodoethyl ether.

Action of propyl iodide upon sodium di-β-methoxyethylphosphite. The lower layer was separated in this reaction as specified above and then heated in vacuo at high temperature. A small quantity of liquid products distilled, though they could not be identified because of the minute quantity involved. The residue left in the flask was a white mass that contained no halogen and deliquesced in air. The residue was analyzed and found to be the sodium salt of the methoxyethyl ester of propylphosphinic acid.

0.0858 g, 0.1529 g substance: 23.3 ml, 42.0 ml 0.5 N NaOH. Found %: P 15.01, 15.21. $C_6H_{14}O_4PNa$. Calculated %: P 15.19.

Action of iodobenzene upon sodium di-β-methoxyethylphosphite. The lower layer formed in the reaction of iodobenzene with sodium di-β-methoxyethylphosphite as specified above was a thick, heavy liquid that was insoluble in benzene. The benzene used in the solubility tests was driven off. Benzene

was poured over the reaction product and then driven off over and over until a Beilstein test of the residue showed it contained no more halogen. After all the benzene had been driven off in vacuum, the residue was an extremely tacky mass that deliquesced in air; it was analyzed and found to be the sodium salt of the methoxyethyl ester of phenylphosphinic acid.

0.1258 g, 0.0954 g substance: 31.3 ml, 23.3 ml 0.5 N NaOH. Found %: P 13.75, 13.55. $C_8H_{12}O_4PNa$. Calculated %: P 13.0.

Action of allyl iodide upon sodium di-β-methoxyethylphosphite. 4.2 grams (0.5 mole) of allyl iodide were poured into sodium di-β-methoxyethylphosphite, prepared from 1.2 g of metallic sodium and 9.6 g of di-β-methoxyethylphosphorous acid. The turbidity caused by the addition of the allyl iodide quickly settled to the bottom of the flask as a heavy, viscous liquid. The ether solution was decanted. The ether was driven out of the lower layer by heating in vacuo on a water bath to 35-40°, and then the lower layer was analyzed.

0.1522 g, 0.1390 g substance: 27.7 ml, 25.2 ml 0.5 N NaOH. 0.1522 g, 0.1390 g substance: 0.0545 g, 0.0501 g AgI. Found %: P 10.06, 10.03; I 19.3, 19.6. $C_{15}H_{33}O_{10}P_2Na_2I$. Calculated %: P 10.19; I 20.8.

The analysis for iodine was done in the filtrate after the phosphorus had been determined.

SUMMARY

1. The action of iodine derivatives upon a sodium dialkylphosphite results in an addition reaction, followed by the splitting out of either sodium iodide or an alkyl iodide. The alkyl group is split out of the ester group.

2. Equations are proposed for these reactions.

3. The action of allyl iodide upon a sodium dialkylphosphite results in the addition of the allyl iodide to the sodium dialkylphosphite, followed by addition of the sodium dialkylphosphite at the allyl double bond.

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THE REACTION OF AZLACTONES (OXAZOLONES) WITH THIOACETIC ACID

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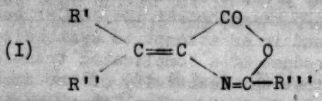
Thiols [1], hydrogen sulfide [2], and thioacetic acid [3] are added to α,β- unsaturated carboxylic acids, yielding the respective β-thio derivatives of the acids. The thiols and hydrogen sulfide are added when catalysts are present: alkalies, bases, acid peroxides, ascaridole [4], etc. Thioacetic acid is added relatively easily to unsaturated [3] acids, particularly when a nitro group is attached to the α-carbon atom of the acid [5], thus increasing the reactivity of the double bond. The presence of an acylamino group attached to the α-carbon atom diminishes the reaactivity of the double bond, so that catalysts are required to produce a reaction between unsaturated acylamino acids and thioacetic acid [4]. The thiols are also added to compounds of the following type:



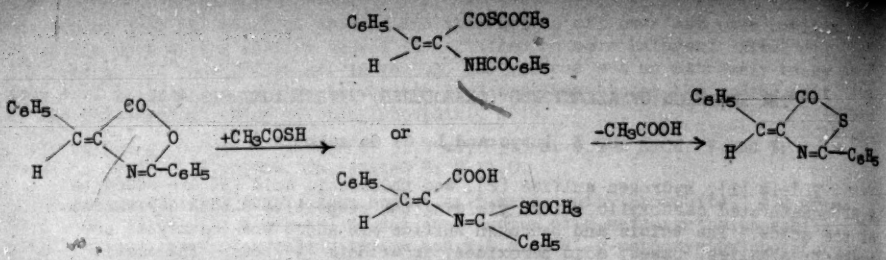
(I)

i.e., to azlactones of unsaturated α-acylamino acids; it has been shown [6] that thiophenol is added both at the >C=C< bond and to the azlactone ring, first opening the latter.

The present paper is a study of the addition of thioacetic acid to two azlactones: 2-phenyl-4-benzyliden-5-oxazolone and 2-phenyl-4-isopropyliden-5-oxazolone. The difference between these two azlactones is in the radicals in the group attached at the 4 position.

Reacting thioacetic acid with 2-phenyl-4-benzyliden-5-oxazolone yielded a compound with the empirical formula $C_{18}H_{11}ONS$. If two molecules of thioacetic acid had been added to the azlactone, the empirical formula would have been $C_{20}H_{19}O_4NS_2$. If the molecule of thioacetic acid had been added only at the >C=C< double bond or only after previous opening of the azlactone ring, we would have had a compound with the formula $C_{18}H_{15}O_3NS$. The compound we secured had no active hydrogen atoms [7]. Its reaction for a sulfhydryl group was negative. Heating in an alkali yielded an acid with the empirical formula of $C_{10}H_{13}O_2NS$. This acid possessed two active hydrogen atoms; heating it with acetic anhydride yielded the original compound again. When our compound was reacted with piperidine, it yielded a piperidide of the corresponding acid. A study of the properties of the substance we had synthesized forced us to conclude that the thioacetic acid did not react with the 2-phenyl-4-benzyliden-5-oxazolone at the >C=C< bond but rather with the azlactone ring, involving addition to the previously opened azlactone ring as well as a subsequent splitting off of a molecule of acetic acid, accompanied by formation of a thiazolone ring. The supposed reaction may be represented as follows: (See top of next page).

To prove that our conjecture was correct, we decided to react thioacetic acid with an azlactone that had no >C=C< ring, namely, 2-phenyl-4-benzyl-5-oxazolone. This yielded a compound with the empirical formula $C_{16}H_{13}ONS$, which had no active hydrogen atoms and exhibited a negative reaction for the SH group. This compound yielded a piperidide of corresponding acid with piperidine, which proved that this reaction followed the same course as in the case of the 2-phenyl-4-benzyliden-5-oxazolone, i.e., as outlined above.



When we reacted thioacetic acid with 2-phenyl-4-isopropyliden-5-oxazolone, we secured two compounds. One compound, with the empirical formula $C_{14}H_{15}O_3NS$, was secured when the azlactone was heated with the theoretical quantity of thioacetic acid. The other compound, with the empirical formula $C_{23}H_{26}O_2N_2S$, was secured either by heating the azlactone for a long time with an excess of thioacetic acid or by distilling the first compound in vacuo at 4-6 mm residual pressure. The first compound was the product of the addition of thioacetic acid to the 2-phenyl-4-isopropyliden-5-oxazolone at the >C=C< bond. American researchers secured a similar compound in an attempt to synthesize penicillin [8]. The second compound was the product of a complicated transformation of the first one. We see, therefore, that the reactivity of the double bond is affected by the nature of the radicals in the group at the 4 position, and, judging from the nature of the end products we secured, we may conclude that the double bond in 2-phenyl-4-benzyliden-5-oxazolone is less reactive than the double bond in 2-phenyl-4-isopropyliden-5-oxazolone.

EXPERIMENTAL

I. 2-Phenyl-4-benzyliden-5-thiazolone. 5 g of 2-phenyl-4-benzyliden-5-oxazolone and 4 g of thioacetic acid (98-99%) were heated together on a water bath for 18 hours in a round-bottomed flask fitted with a reflux condenser with a calcium chloride tube. Then the reaction mass was allowed to cool, and 15 ml of alcohol was added; crystals settled out. They were filtered out, washed with alcohol, and recrystallized from a 1:1 mixture of benzene and alcohol. This yielded lemon-yellow crystals of 2-phenyl-4-benzyliden-5-thiazolone with a m.p. of 132-133°. They were freely soluble in benzene, sparingly soluble in alcohol, and insoluble in alkalies. The yield was 54% of the theoretical.

Found %: C 72.51; H 4.35; N 5.28; S 11.95. $C_{18}H_{11}ONS$. Calculated %: C 72.45; H 4.15; N 5.28; S 12.07.

II. Hydrolysis of 2-phenyl-4-benzyliden-5-thiazolone. 2 grams of 2-phenyl-4-benzyliden-5-thiazolone were boiled for two hours with 30 ml of 1N sodium hydroxide. When heating was complete, the solution was cooled, 20 ml of ether were added, and the whole was neutralized with 10% hydrochloric acid. The mixture was thoroughly shaken, the ether layer decanted, the aqueous layer extracted with ether three times, and the ether extracts combined with the initial ether solution. The ether solution was twice washed with ice water and desiccated with sodium sulfate. The ether was driven off, and the residue left behind was crystallized twice from benzene. This yielded α-thiobenzoylaminocinnamic acid, a white crystalline substance that was freely soluble in alcohol, benzene, and ether. M.p. 136-137°.

Found %: C 68.01; H 4.79; N 5.09; S 11.38; M 280.2. $C_{18}H_{13}O_2NS$. Calculated %: C 67.84; H 4.59; N 4.95; S 11.30; M 283.1.

1 gram of α-thiobenzoylaminocinnamic acid was heated for 20 minutes with 5 ml of acetic anhydride. As the reaction mass cooled, yellow crystals settled out; their m.p. was 132-133° after recrystallization from a benzene-alcohol mixture. The mixed melting point with 2-phenyl-4-benzyliden-5-thiazolone exhibited no depression. The yield was 85% of the theoretical.

III. The piperidide of α-thiobenzoylaminocinnamic acid. 5 g of piperidine were added to 1 g of 2-phenyl-4-benzyliden-5-thiazolone, causing the deposit to dissolve and the reaction mass to warm up. Then the solution was heated for 20 minutes. As it cooled, a white crystalline precipitate settled out. It was filtered out, washed with petroleum ether, and twice recrystallized from 70% alcohol. M.p. 138-139°. The yield was 60% of the theoretical.

Found %: C 72.20; H 6.57; N 8.0; S 8.92. $C_{21}H_{22}ON_2S$. Calculated %: C 71.97; H 6.38; N 7.99; S 9.14.

IV. 2-Phenyl-4-benzyl-5-thiazolone. 2 grams of 2-phenyl-4-benzyl-5-thiazolone, prepared by heating α-N-benzoylphenylalanine with acetic anhydride, were heated with 2 g of thioacetic acid to 95-100° for 18 hours. The excess thioacetic acid was then driven off in vacuo at 10 mm. The substance left behind after the thioacetic acid had been driven off was crystallized twice from ether. M.p. 110-112°.

Found %: C 71.78; H 5.02; N 5.24; S 12.20. $C_{16}H_{13}ONS$. Calculated %: C 71.91; H 4.91; N 5.24; S 11.98.

V. The piperidide of α-thiobenzoylaminohydrocinnamic acid. 0.5 gram of 2-phenyl-4-benzyl-5-thiazolone was dissolved in 2.5 g of piperidine and then heated on a water bath for 20 minutes. As it cooled, crystals settled out. They were filtered out, washed with petroleum ether, and crystallized from alcohol: m.p. 172-173°.

Found %: N 7.98; S 8.98. $C_{21}H_{24}ON_2S$. Calculated %: N 7.96; S 9.10.

VI. Reaction of thioacetic acid with 2-phenyl-4-isopropyliden-5-oxazolone. 5 grams of 2-phenyl-4-isopropyliden-5-oxazolone were heated with 2.5 g of thioacetic acid on a water bath for 6 hours. The entire mass crystallized upon cooling. The substance sublimed when the flask was gently warmed at 1 mm residual pressure. The sublimate had a m.p. of 99-101°.

Found %: C 60.85; H 5.68; N 4.98; S 11.70. $C_{14}H_{15}O_3NS$. Calculated %: C 60.65; H 5.42; N 5.05; S 11.55.

The substance distilled when heated in vacuo at 4-6 mm. It rapidly solidified into a pale pink mass. The mass was dissolved in alcohol, and white crystals with a m.p. of 98-99° were thrown down with water.

Found %: C 70.49; H 6.9; N 7.20; S 8.46. $C_{23}H_{26}O_2N_2S$. Calculated %: C 70.05; H 6.61; N 7.10; S 8.12.

All analyses were performed by E. A. Ignatyeva, to whom we are deeply grateful.

SUMMARY

1. Thioacetic acid reacts with 2-phenyl-4-benzyliden-5-oxazolone at the azlactone ring rather than at the >C=C< bond, yielding the corresponding thiazolone derivative.

2. Thioacetic acid reacts with 2-phenyl-4-isopropyliden-5-oxazolone at the >C=C< double bond.

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THE CONDENSATION OF DIMETHYLANILINE WITH ALKYL (OR ARYL) HALIDES

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Heating pyridine with 2,4-dinitrochlorobenzene yields a quaternary ammonium compound, the subsequent conversions of which have been investigated by several researchers [1]. Pyridine also readily forms a quaternary ammonium compound with β-bromoethyl-phthalimide (see the experimental section). Investigation of the condensation of these halogen derivatives with dimethylaniline has shown that the reaction with pyridine does not take place under the conditions that yield a coordination compound. Only at 100° does an ionogenic halogen atom appear, but then the reaction mixture at once turns a violet-blue. A sample exhibits the characteristic reaction for methyl violet, evidence of the formation of formaldehyde in the reaction mixture. According to our previous paper [2], formaldehyde may be formed as the result of oxidation of the methyl ion split out of the corresponding quaternary ammonium compound. The formation of N-methyl-N-phenyl-2,4,-dinitroaniline when 2-4-dinitrochlorobenzene was used and of β-(N-methyl-N-phenyl)-aminoethylphthalimide in the condensation with β-bromoethylphthalimide, as well as the appearance of the color that is characteristic of methyl violet, forces us to conclude that dimethylaniline condenses with alkyl (or aryl) halides in the same way as it does with acid halides, and that, therefore, a quaternary ammonium compound must be formed as the initial reaction product.

EXPERIMENTAL

I. N-methyl-N-phenyl-2,4-dinitroaniline. a) Condensation of dimethylaniline with 2,4-dinitrochlorobenzene. 3 grams of 2,4-dinitrochlorobenzene were dissolved in 1.5 g of dimethylaniline (free of any traces of monomethylaniline). The solution was dark red. It was heated carefully to 100°. At that temperature the reaction for an ionogenic halogen atom was positive, the solution turning violet and a sample exhibiting the characteristic reaction for methyl violet. When the reaction mass had cooled, it was poured into a 1% solution of hydrochloric acid, an oil settling out. The oil was washed with a 5% alkali and with water and then set aside to stand.

The oil crystallized within 20-25 hours. The crystals were squeezed out, washed with alcohol, and crystallized from alcohol. The N-methyl-N-phenyl-2,4,-dinitroaniline consisted of lustrous orange-red crystals with a m.p. of 166-167.5°. The yield was 92% of the theoretical.

Found %: C 57.34; H 4.36; N 15.39. $C_{13}H_{11}O_4N_3$
Calculated %: C 57.12; H 4.06; N 15.36.

b) Condensing monomethylaniline with 2,4-dinitrochlorobenzene. 3 grams of monomethylaniline were heated on a water bath with 1.5 g of 2,4-dinitrochlorobenzene for 25-30 minutes. Then the mixture was cooled, all of it crystallizing. The crystals were diluted with a small amount of alcohol, filtered out, washed on the filter with alcohol, and crystallized from alcohol. Orange-red crystals with a m.p. of 166-167.5°. Their mixed melting point with N-methyl-N-phenyl-2,4-dinitroaniline exhibited no depression.

Found %: C 57.21; H 4.16; N 15.29. $C_{13}H_{11}O_4N_3$.
Calculated %: C 57.12; H 4.06; N 15.36.

II. Coordination compound of β-bromoethylphthalimide with pyridine. 3 grams of anhydrous pyridine were heated with 5 g of β-bromoethylphthalimide on a water bath. After a few minutes had elapsed, the solution became transparent and slightly

yellowish, crystallizing immediately thereafter. It was cooled, and the crystals were quickly washed with absolute ether and dried in a desiccator over phosphorus pentoxide.

Found %: C 53.82; H 3.99; N 8.46; Br 24.28. $C_{15}H_{13}O_2N_2Br$.
Calculated %: C 54.04; H 3.93; N 8.41; Br 24.02.

III. Condensation of dimethylaniline with β-bromoethylphthalimide. 2.5 grams of dimethylaniline were freed of all traces of monomethylaniline, heated to 100° with 1.5 g of β-bromoethylphthalimide, and kept at that temperature for 10 hours. The reaction mass gradually turned blue. After it had cooled, the reaction mass was poured into a 1% solution of hydrochloric acid, and the oil was separated, washed with water and triturated with alcohol. Yellow crystals with a m.p. of 105-107° settled out after the oil had been allowed to stand for a long time (from 1 to 20 hours). The melting point of β-(N-methyl-N-phenyl)-aminoethylphthalimide was 107-109° after it had been recrystallized from alcohol. The yield was 15-20% of the theoretical.

Found %: C 72.56; H 5.91; N 10.03. $C_{17}H_{16}O_2N_2$.
Calculated %: C 72.82; H 5.8 ; N 10.0:

Heating the reaction mass for upwards of 20 hours yielded N-di(ethylphthalimide)-aniline with a m.p. of 207-210°.

Found %: C 70.57; H 4.55; N 9.57; $C_{28}H_{21}O_4N_3$.
Calculated %: C 71.04; H 4.82; N 9.56.

IV. Condensation of monomethylaniline with β-bromoethylphthalimide. The monomethylaniline was condensed with the β-bromoethylphthalimide both in pyridine and without it. The same substance, β-(N-methyl-N-phenyl)-aminoethylphthalimide, was secured in both instances.

3 grams of monomethylaniline, 3 g of β-bromoethylphthalimide, and 2 g of pyridine were heated until the reaction mass boiled gently for 1 hour. When the mass had cooled, it was poured into a 1% solution of hydrochloric acid and then extracted with ether. The ether solution was washed 2 or 3 times with a 1% solution of hydrochloric acid and then with water until its reaction was neutral. The ether extract was desiccated with Glauber's salt, and the ether then driven off. The remaining crystalline yellow substance was twice recrystallized from alcohol. M.p. 107-109°. The yield was 70-75% of the theoretical.

Found %: C 72.71; H 5.98; N 10.10. $C_{17}H_{16}O_2N_2$.
Calculated %: C 72.82; H 5.80; N 10.00.

The methyl groups are replaced by an ethylphthalimide group after prolonged boiling, as was the case in the condensation with dimethylaniline.

All analyses were performed by E.A.Ignatyeva, to whom we are deeply indebted.

SUMMARY

1. The reaction of dimethylaniline with 2,4-dinitrochlorobenzene or with β-bromoethylphthalimide sets in only at 100°.

2. Methyl violet is produced in addition to the principal reaction products, which forces one to assume that the reaction involved in the condensation of dimethylaniline with alkyl (or aryl) halides resembles the condensation of dimethylaniline with acid halides.

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A NEW METHOD OF SYNTHESIZING THIOACETYLCHOLINE IODIDE

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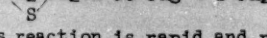
Thioacetylcholine iodide, the sulfur analog of acetylcholine iodide, is widely employed in various biochemical investigations. The multistage method of preparing thioacetylcholine iodide described in the literature cannot satisfy the growing demand for this product, however.

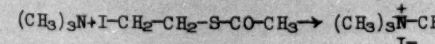
In Renshaw's method [1], for instance, the initial product used for the synthesis is dimethylaminoethanol, in which the hydroxy group is replaced by chlorine by the usual method. The 2-chloroethyldimethylamine is heated with thiourea, the resulting addition product being hydrolyzed with dilute alkali. The 2-mercaptoethyldimethylamine produced is converted by the action of acetyl chloride into 2-(acetthio)-ethyldimethylammonium chloride. The latter compound is treated with an excess of silver hydroxide to produce the free base. In the last stage of the synthesis the 2-(acetthio)-ethyldimethylamine is treated with an excess of methyl iodide, yielding thioacetylcholine iodide. In Renshaw's description of this method of producing thioacetylcholine iodide, he comments on the high yield of the end product, but when we repeated his synthesis we failed to get any such yield.

The method we have worked out for producing thioacetylcholine iodide involves only two stages: 1) synthesis of the 2-iodothioethyl ester of acetic acid; and 2) reacting that ester with trimethylamine. The 2-iodothioethyl ester of acetic acid is prepared by the method described in one of the patents covering acid halides of carboxylic acids [2] and by a reaction of acetyl iodide with ethylene sulfide we had developed:



This reaction is rapid and produces a high yield (70-75%) of the 2-iodothioethyl ester of acetic acid, which is not described in the literature.

The thioacetylcholine iodide is produced by reacting the 2-iodothioethyl ester of acetic acid with trimethylamine:



in anhydrous ether in the cold. The end product of the reaction gradually settles out of the solution as a colorless, heavy mass of crystals. Double recrystallization from n-propyl alcohol produces a satisfactory yield (70-75%) of the pure thioacetylcholine iodide.

EXPERIMENTAL

Preparation of the 2-iodothioethyl ester of acetic acid. 17 grams of acetyl iodide and 25 ml of anhydrous carbon tetrachloride were placed in a round-bottomed flask fitted with a reflux condenser and a dropping funnel. Then 6 g of ethylene sulfide were added slowly to the solution from the dropping funnel. When addition was complete, the reaction mixture was heated on a water bath at 40-50° for 30 minutes. Then the solvent was driven off, and the 2-iodothioethyl ester of acetic acid remaining was distilled in vacuo. B.p. 97° (10 mm). Yield: 17 g.

d_4^{17} 1.8195; n_D^{17} 1.5190; MR_D 38.536; calc. 38.273. 0.5012 g substance: 0.4881 g $BaSO_4$; 0.5115 g AgI. Found %: I 55.23; S 13.41. C_4H_7OSI. Calculated %: I 54.9; S 13.86.

Synthesis of thioacetylcholine iodide. 16 g of the 2-iodothioethyl ester of acetic acid and 35 ml of anhydrous ether were placed in a 150-ml wide test tube fitted with a ground-glass stopper. The 5 g of chilled liquid trimethylamine were added in small batches to the solution, chilled to -10 and -15°, the test tube being stoppered and agitated after the addition of each batch of trimethylamine. After the addition was complete, the reaction mixture was allowed to stand in the cold for 3-4 hours and then at room temperature for another 2-3 hours. The resultant thioacetylcholine iodide was suction-filtered and crystallized from a small quantity of propyl alcohol. This yielded lustrous crystals with a m.p. of 204-205°. The yield was 80%.

Found %: I 43.75; S 10.88; N 4.67. $C_7H_{16}NOSI$.
Calculated %: I 43.95; S 11.09; N 4.83.

SUMMARY

1. A new and convenient method has been found for producing thioacetylcholine iodide, involving the addition of the 2-iodothioethyl ester of acetic acid to trimethylamine in the cold.

2. The 2-iodothioethyl ester of acetic acid has been synthesized for the first time by reacting ethylene sulfide with acetyl iodide and has been described.

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ARYL TRICHLOROPHOSPHAZOSULFONES

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Not very many compounds containing the phosphazosulfone group, $SO_2-N=P\equiv$ are known. Remsen and his associates [1] synthesized p-trichlorophosphazosulfonebenzoyl chloride $Cl_3P=N-SO_2-C_6H_4-COCl(p)$ by reacting p-sulfaminobenzoic acid with phosphorus pentachloride. Rodionov and Yavorskaya [2] synthesized the same compound by reacting phosphorus pentachloride with the calcium salt of p-sulfaminobenzoic acid. The acid chloride of trichlorophosphazosulfuric acid, $ClSO_2-N=PCl_3$, has recently been produced [3] by reacting sulfaminic acid with phosphorus pentachloride. Up to the present, therefore, only two compounds are known, the molecules of which contain the phosphazosulfone group: Remsen's acid chloride and the acid chloride of trichlorophosphazosulfuric acid. The interesting question arose of whether the phosphazosulfone group, $SO_2N=P\equiv$, is a singular phenomenon or can be introduced into other molecules as well. The aryl sulfamides are the most convenient substances for solving this problem. If the phosphazosulfone group is stable, the action of phosphorus pentachloride upon the aryl sulfamides ought to yield trichlorophosphazosulfonamides in a reaction resembling the one in which the acid chloride of trichlorophosphazosulfuric acid was synthesized:

$$NH_2SO_2OH + 2PCl_5 \longrightarrow 3HCl + POCl_3 + ClSO_2N = PCl_3$$

$$Ar-SO_2NH_2 + PCl_5 \longrightarrow 2HCl + Ar-SO_2N = PCl_3.$$

Fittig, in 1858, was the first one to investigate the action of phosphorus pentachloride upon aryl sulfamides [4]. He found that the aryl sulfamides react readily with phosphorus pentachloride when they are heated gently, yielding substances that regenerate the initial sulfamide when acted upon by water. Fittig advanced the hypothesis that the structure of the substances produced resembled that of the imidochlorides, though he cited nothing in support of this conjecture. Fittig did not isolate any individual substances. Gerhardt made a study of the reaction of phosphorus pentachloride with benzenesulfonamide in that same year [5]. He reported that the reaction involved the liberation of phosphorus oxychloride; hence, a product analogous to an imidochloride was formed. Gerhardt did not isolate the reaction product in the pure state. Reacting the reaction product with ammonium carbonate, Gerhardt secured the ammonium salt of an unknown acid. When this salt was reacted with hydrochloric acid, it yielded a "new amide," which Gerhardt believed to be a product whose structure was similar to that of an amidine, i.e., $C_6H_5-SO(=NH)(NH_2)$, which possessed the properties of a strong acid. In 1869 Wichelhaus checked Gerhardt's findings [6]. He could not secure the "new amide" and asserted that this substance did not exist. Wichelhaus then showed that no phosphorus oxychloride is liberated when a mixture of an aryl sulfamide and phosphorus pentachloride is heated, even as high as 180° (Gerhardt expelled phosphorus oxychloride at 150°), and that the reaction product contained phosphorus. Wichelhaus recovered a substance with a m.p. of 130-131°, whose composition (C,H,S,N,P, and Cl) was that of $C_6H_5SO_2NHPCl_2$, from the reaction mixture, the yield being low, apparently (he does not state the yield). Thus, it is Wichelhaus' opinion that the reaction is given by the equation:

$$C_6H_5SO_2NH_2 + PCl_5 \longrightarrow Cl_2 + HCl + C_6H_5SO_2NHPCl_2.$$

The evolution of free chlorine was demonstrated, but Wichelhaus believed that part of the chlorine entered into the reaction, laying the foundation for oily by-products. In 1875 Wallach and Huth [7] made a study of the reaction of aryl sulfamides with phosphorus pentachloride. They found that the reaction sets in at 100° and that no liquid products separate up to 160°. Wallach and Huth confirmed the evolution of free chlorine, but they demonstrated that the amount of chlorine evolved is

extremely small, not exceeding the amount of chlorine liberated when pure phosphorus pentachloride is heated under approximately the same conditions. Wallach and Huth therefore doubted that free chlorine was evolved in the reaction, especially as the reaction product had a "homogeneous appearance," and it was hard to assume that it contained impurities produced by such large quantities of chlorine. Despite the "homogeneous appearance," of the reaction product, Wallach and Huth were unable to recrystallize it " owing to its great variability," though they do state that the reaction product contained more chlorine after having been washed with petroleum ether than called for by Wichelhaus' formula, i.e., $C_6H_5SO_2NHPCl_2$. Wallach and Huth conclude: "apparently, the reaction of phosphorus pentachloride with sulfamides is more complicated than appears from Wichelhaus' simple equation."

Thus the references in the literature are indeterminate, highly contradictory, and justify the assumption that the reaction of phosphorus pentachloride with aryl sulfamides is a complex one, the reaction products being highly variable, and their isolation in the pure state entailing considerable experimental difficulty. Therefore, in making a fresh start on the investigation of the reaction between phosphorus pentachloride and the aryl sulfamides, the present author expected, at best, to obtain the sought-for aryl trichlorophosphazosulfones, even though the yields were low. How great was his surprise at the results of his very first tests: the reaction was practically quantitative, in accordance with the following equation:

$$ArSO_2NH_2 + PCl_5 \longrightarrow ArSO_2N{=}PCl_3 + 2HCl$$

at the temperature of a boiling water bath, the reaction time being 20-60 minutes. When equimolecular quantities of pure substances were used for the reaction, the amount of hydrogen chloride liberated corresponded to the foregoing equation within 0.5%. The amount of chlorine liberated was negligible. No volatile liquids were found. The composition and the molecular weight of the reaction product, without any refining, conformed precisely to the composition and molecular weight of the aryl trichlorophosphazosulfone. The melting points of the "crude" aryl trichlorophosphazosulfones were only 1-2° below those of the doubly recrystallized products. The reaction is especially smooth when a small quantity of carbon tetrachloride is present, though it is nearly quantitative even without carbon tetrachloride in the case of the low-melting aryl trichlorophosphazosulfones. Upon hydrolysis, the reaction products yield hydrogen chloride, phosphoric acid, and an aryl sulfamide, in exact accordance with the following equation:

$$ArSO_2N{=}PCl_3 \xrightarrow{+H_2O} ArSO_2NH_2 + 3HCl + H_3PO_4.$$

All these facts are sufficiently convincing proof that the reaction of phosphorus pentachloride with the aryl sulfamides actually conforms to the foregoing equation, and that the reaction products actually have the structure of aryl trichlorophosphazosulfones. How can we explain the failure of all the previous researches? It was probably due to the fact that the initial substances employed in the original experiments were not pure enough, and the end product of the reaction was contaminated with by-products. Once we know the properties of the aryl trichlorophosphazosulfones, however, we can successfully secure them from the technical products.

Hence, most of the findings of Fittig, Gerhardt, Wichelhaus, and Wallach are wrong. Likewise wrong is Wallach's assertion that the reaction between phosphorus pentachloride is more complicated than Wichelhaus' simple equation. In reality, the equation for this reaction is even simpler than Wichelhaus' equation, being irreversible and nearly quantitative.

The aryl trichlorophosphazosulfones are crystalline substances that are either odorless or with a very faint odor of their own. They are readily soluble in benzene, ether, acetone, acetic acid, and carbon tetrachloride, and slightly soluble in

petroleum ether. The aryl trichlorophosphazosulfones react rather slowly with water. A 0.2 g sample, for example, dissolves completely only after 40 minutes of agitation at room temperature in 100 ml of water containing 10 ml of 1N alkali. The slowness of hydrolysis is probably due to the slight solubility in water, since the addition of a small amount of alcohol causes hydrolysis to set in rather violently. When aryl trichlorophosphazosufones are exposed to the air, they change slowly, giving off hydrogen chloride in a reaction with atmospheric moisture. The aryl trichlorophosphazosulfones react vigorously with ammonia, primary and secondary amines, alcohols, and phenols. When aryl trichlorophosphazosulfones are added to ethyl alcohol, the mixtures begins to foam.

Aryl trichlorophosphazosulfones cannot be distilled without decomposing at atmospheric pressure or when the pressure is reduced to 6 mm. They can be refined by recrystallization from concentrated solutions in carbon tetrachloride, in petroleum ether, or in a mixture of these two solvents. There is no need for this refining, however, since analytically pure substances are secured directly from the reaction when completely anhydrous and pure sulfamides and laboratory-made phosphorus pentachloride are utilized.

EXPERIMENTAL

Quantitative test. 0.1 mole of the pure anhydrous amide of o-toluenesulfonic acid (17.12 g) was mixed with 0.1 mole of pure phosphorus pentachloride (20.83 g) in a round-bottomed flask with a fused-on reflux condenser and a fused-on tube to drive the hydrogen chloride off with nitrogen after the test was over. The condenser was connected to three absorbers via tubes whose ends were 5 mm above the level of the liquid. The first absorber contained 200 ml of a 1N alkali solution, while the second and third each contained 100 ml of the same solution. The absorbers were cooled with ice water during the test. The flask was immersed in a boiling water bath. The evolution of hydrogen chloride set in at once, as indicated by the "currents" in the liquid within the first absorber. Within 15 minutes the mixture began to liquefy, and the evolution of hydrogen chloride was accelerated. A rather large quantity of sublimed phosphorus pentachloride was deposited within the reflux condenser; it was washed off with the reaction mixture by suitably tilting and shaking the flask. Within 40 minutes the reaction mixture had turned into a transparent colorless, water-white liquid. After 60 minutes, the hydrogen chloride was expelled from the flask with nitrogen, and heating was stopped. When the flask had cooled, its contents crystallized completely into a solid, brittle, entirely dry mass of prismatic crystals. The residue left within the flask weighed 30.68 g, or 100.1% of the theoretical. After the residue had been dried in vacuo at 100 deg for 15 minutes, it weighed 30.53 g, or 99.6% of the theoretical. This decrease in weight is probably due to the fact that the reaction product dissolved hydrogen chloride, or else to the phosphorus pentachloride having contained some phosphorus oxychloride, despite all the precautions taken, the pentachloride going off only when heated in vacuo. The contents of the absorbers were transferred quantitatively to a weighed flask, and the weight of the solution was increased to 1000.0 grams. Then the acidity and the free chlorine were determined in the solution in the usual way.

500.0 g solution: 2.1 ml 0.1N hyposulfite; 100.0 g solution: 20.1 ml 1N acid. Found: 0.0073 g free chlorine; hydrogen chloride 0.199 equivalent. Calculated for the specified equation: 0.0000 g chlorine; 0.200 equivalent hydrogen chloride.

The amount of chlorine liberated is less than that evolved by the same quantity of phosphorus pentachloride during the same time and under approximately the same conditions so that the free chlorine evolved bears no relation to the principal reaction. The hydrocarbon produced is 99.5% of the theoretical.

It should be noted that carefully vacuum-dried, chemically pure o-toluenesulfamide and pure, preferably laboratory-made phosphorus pentachloride, carefully "dried" in vacuo, must be used. All weighing must be done in a dry chamber. If these prerequisites are not observed, the yields of the reaction products will vary by 1-2%.

The preparative reaction. Equimolecular quantities of the vacuum-dried arylsulfamide and the chemically pure phosphorus pentachloride (preferably prepared in the laboratory) are mixed in a round-bottomed flask, which is terminated by a reflux condenser, the upper end of which is connected to an absorber for hydrogen chloride. The phosphorus pentachloride need not be pulverized. 100 ml of anhydrous carbon tetrachloride are added to the mixture for each mole of the arylsulfamide, and the mixture is heated on a boiling water bath. The evolution of hydrogen chloride sets in at once. The mixture is liquefied within 10-20 minutes, and turns into a homogeneous, transparent, colorless liquid within 20-40 minutes. The reaction is complete after 60 minutes have elapsed. The carbon tetrachloride is driven off in a 5-6 mm vacuum at the temperature of the boiling water bath, after which the reaction product is kept at that same temperature in vacuo for another 15-20 minutes to expel all the hydrogen chloride and the volatile phosphorus compounds that are formed during the weighing and addition of the phosphorus pentachloride. If an excess of phosphorus pentachloride should happen to be used, heating in vacuum is continued until no more phosphorus pentachloride sublimes.

The reaction product is poured into a porcelain dish while still liquid and placed in a desiccator. If the substance is to be recrystallized at once, for which there is ordinarily no need, the requisite quantity of carbon tetrachloride is added to the still molten product, and the solution is set aside to crystallize. In the case of tolyl p-trichlorophosphazosulfone, for example, 200 ml of carbon tetrachloride is added per mole, a yield of 89.2% of the trichloride being secured as large colorless prisms after suction-filtering and washing (with 3 batches of 70 ml of carbon tetrachloride).

The yields of the unrecrystallized aryl trichlorophosphazosulfones average 97-99% of the theoretical.

Properties and analyses of some aryl trichlorophosphazosulfones.[1] The yield of phenyl trichlorophosphazosulfone was approximately 99%. It crystallized in aggregates of elongated needles. The crude product had a m.p. of 53.5° (maximum, thermometer bulb in the liquid). The m.p. was 54.5° after two recrystallizations from carbon tetrachloride or petroleum ether. There is practically no difference between the analysis results of the "crude" and the recrystallized substance, so that the only figures we cite are those for the analyses of the "crude" substance.

52.72 mg substance: 47.18 mg CO_2; 8.05 mg H_2O; 54.33 mg substance: 48.71 mg CO_2; 8.20 mg H_2O; 0.1952 g substance: 0.1562 g $BaSO_4$; 0.1693 g substance: 0.1341 g $BaSO_4$; 44.47 mg substance: 1.53 ml 0.1 N acid; 36.76 mg substance: 1.27 ml 0.1 N acid; 0.2980 g substance: 0.1123 g $Mg_2P_2O_7$; 0.3244 g substance: 0.1232 g $Mg_2P_2O_7$; 0.0955 g substance: 0.1407 g AgCl; 0.1035 g substance: 0.1521 g AgCl; 0.6561 g substance: 11.25 ml 1 N alkali; 0.6828 g substance: 11.70 ml 1 N alkali; 0.1242 g substance; 15.0 g benzene: Δt 0.149°; 0.2516 g substance; 15.0 g benzene: Δt 0.299°. Found %: C 24.40, 24.45; H 1.71, 1.69; S 10.99, 10.87; N 4.82, 4.84; P 10.50, 10.58; Cl 36.43, 36.34; acid

[1] See the theoretical section for the common properties.

equivalent in hydrolysis 5.014, 5.012; M 285.6, 288.3. $C_8H_5O_2NCl_3SP$. Calculated %: C 24.61; H 1.72; S 10.96; N 4.79; P 10.60; Cl 36.37; acid equivalent in hydrolysis 5.000; M 292.50.

The yield of tolyl o-trichlorophosphazosulfone was about 98%. Large colorless, transparent prisms after recrystallization from a small quantity of carbon tetrachloride; m.p. of the "crude" 52.5° (maximum); m.p. of the recrystallized product 53.5°. The analysis data are given only for the recrystallized substance.

53.21 mg substance: 53.26 mg CO_2; 11.04 mg H_2O; 0.7739 g substance: 12.65 ml 1 N alkali; 0.1437 g substance; 15.0 g benzene: Δt 0.165°, 0.2964 g substance; 15.0 g benzene: Δt 0.336°. Found %: C 27.30; H 2.32; acid equivalent in hydrolysis 5.009; M 298.4, 302.4. $C_7H_7O_2NCl_3SP$. Calculated %: C 27.41; H 2.30; acid equivalent in hydrolysis 5.000; M 306.51.

The yield of tolyl p-trichlorophosphazosulfone was 97-99% of the theoretical. Carbon tetrachloride had to be added to the reaction mixture to secure the product, since the reaction mixture did not melt without carbon tetrachloride, and the process would be very slow. It crystallized excellently from carbon tetrachloride in prisms and from petroleum ether in needles. The melting point of the "crude" substance was 104.6° (maximum) and that of the recrystallized product 106.0°. The analysis findings are given only for the "crude" product, since the data for the recrystallized product are practically the same.

53.70 mg substance: 53.73 mg CO_2; 11.28 mg H_2O; 0.8058 g substance: 13.20 ml 1 N alkali; 0.1122 g substance; 15.0 g benzene: Δt 0.131°, 0.2319 g substance; 15.0 g benzene: Δt 0.266°. Found %: C 27.29; H 2.35; acid equivalent in hydrolysis 5.021; M 293.4, 298.7. $C_7H_7O_2NCl_3SP$. Calculated %: C 27.41; H 2.30; acid equivalent in hydrolysis 5.000; M 306.51.

SUMMARY

It has been shown that the data in the literature on the products of the reaction between phosphorus pentachloride and aryl sulfamides are incorrect.

It has been shown that the reaction of phosphorus pentachloride with aryl sulfamides is practically quantitative, yielding aryl trichlorophosphazosulfones.

The properties of some aryl trichlorophosphazosulfones have been described.

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1) See Consultants Bureau English translation, p. 101.

A NEW METHOD OF CONVERTING CARBOXYLIC ACID CHLORIDES INTO THE RESPECTIVE NITRILES

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When trichlorophosphazosulfone-p-benzoyl chloride is distilled in vacuo, phosphorus oxychloride is split out, the nitrogen atom is shifted from the sulfone group to the carboxyl carbon atom, and we get p-benzonitrilesulfonyl chloride [1], as follows:

$$ClCOC_6H_4SO_2N{=}PCl_3 \longrightarrow POCl_3 + NCC_6H_4SO_2Cl.$$

The mechanism of this singular reaction is still unclear. Kemp supposes [2] that the reaction involves a stage in which the trichlorophosphazosulfone-p-benzoyl chloride is polymerized, after which the phosphorus oxychloride is split out and the reaction end product is formed. But this explanation explains nothing. What seems to be more likely is that the reaction occurs in two stages. The first reaction resembles the amidation of carboxylic acids by a sulfonamide [3] or aryl sulfamides [4], as follows:

$$ClCOC_6H_4SO_2N{=}PCl_3 + ClCOC_6H_4SO_2N{=}PCl_3 \longrightarrow ClCOC_6H_4SO_2Cl + Cl_3P{=}NCOC_6H_4SO_2N{=}PCl_3$$

similarly $ArSO_2NH_2 + HOCOR \longrightarrow ArSO_2OH + NH_2COR$ and then

$$Cl_3P{=}NCOC_6H_4SO_2N{=}PCl_3 + ClCOC_6H_4SO_2Cl \longrightarrow 2Cl_3P{=}NCOC_6H_4SO_2Cl.$$

In the second stage, the phosphorus oxychloride is split out, as in the splitting out of sulfuric acid from acyl sulfamic acids [5] or in the splitting out of phosphorus oxychloride from trichlorophosphazosulfuryl chloride [6], as follows:

$$ClSO_2C_6H_4CON{=}PCl_3 \longrightarrow POCl_3 + ClSO_2C_6H_4CN$$

similarly $RCONHSO_2ONH_4 \longrightarrow HOSO_2ONH_4 + RCN$

or $ClSO_2N{=}PCl_3 \longrightarrow POCl_3 + ClSON.$

If these conjectures are correct, there is no need for the $-SO_2N{=}NPCl_3$ and $-COCl$ groups to be in the same molecule. The same reaction ought to take place when halides of carboxylic acids are reacted with any aryl trichlorophosphazosulfone, as follows:

$$RCOCl + ArSO_2N{=}PCl_3 \longrightarrow ArSO_2Cl + [RCON{=}PCl_3]$$

$$[RCON{=}PCl_3] \longrightarrow POCl_3 + RCN.$$

Inasmuch as aryl trichlorophosphazosulfones have become [7] readily available and inexpensive substances, while the carboxylic acid chlorides are readily prepared from the acids and thionyl chloride, as well as by many other methods, this reaction may well serve as a basis for developing a new and convenient way of converting carboxylic acids into their nitriles.

Experiment has confirmed these suppositions. The chlorides of carboxylic acids begin to react with aryl trichlorophosphazosulfones at about 180° the reaction occurring rapidly at 200-220°. Nearly the theoretical quantity of phosphorus oxychloride is driven off within 20 to 30 minutes, what is left in the reaction flask being a mixture of the respective sulfonyl chloride and nitrile, which may be separated by fractionation or otherwise. It is best to process the reaction product with a concentrated aqueous solution of ammonia, then suction-

filtering and washing the nitrile-sulfonamide mixture, and separating the sulfonamide by treating the mixture with a slight excess of a 10% solution of a caustic alkali. Volatile nitriles, such as benzonitrile, may be distilled from the reaction mixture immediately and purified either by fractionation or chemically. This method is especially suitable for the synthesis of high-boiling and comparatively high-melting aromatic nitriles. The nitriles of acids that are decomposed at 200° or undergo changes when acted upon by phosphorus oxychloride cannot, of course, be produced by this method, nor can the nitriles of acids that have low-boiling chlorides. It may be possible, however, to convert the latter into nitriles by carrying the reaction out under pressure. We have been unable, as yet, to secure a high yield of palmitonitrile by this method.

The conversion of acids into nitriles does not require that the carboxylic acid chlorides or the aryl trichlorophosphazosulfones be isolated as such. The carboxylic acid may be mixed with thionyl chloride or phosphorus pentachloride in one flask, and the sulfonamide mixed with the phosphorus pentachloride in the other; the two mixtures are heated for an hour on a water bath, the excess thionyl chloride or the phosphorus oxychloride is driven off, and the two reaction masses are poured into a distillation flask, in which they are heated to 200-220° for 30 minutes and then treated with ammonia or else fractionated. The nitrile yield averages 80-90% of the theoretical, the yields of the sulfonic acid chlorides also running 80-90% of the theoretical. Various aryl trichlorophosphazosulfones may be utilized, but those that are converted into low-melting aryl sulfochlorides are best, since then the reaction with ammonia is accelerated and the reaction mixture is not trapped within the compact solid crystalline mass. Examples and details of the reaction procedure are given in the experimental section.

EXPERIMENTAL

Preparation of benzonitrile from benzoyl chloride and recovery of o-toluene sulfochloride. A mixture of 0.1 mole (30.65 g) of crude tolyl o-trichlorophosphazosulfone and 0.1 mole (14.1 g) of benzoyl chloride was placed in a two-necked round-bottomed flask for distillation. The flask, connected to a receiver that was cooled with ice water, was fitted with two thermometers, the bulb of one being immersed in the reaction mixture and the bulb of the other being in the vapor. The flask was heated on an air bath. The reaction set in at 180 deg, as indicated by the liquid beginning to boil gently, by the expelling of the phosphorus oxychloride, and by the rise of the vapor temperature. The reaction ended 20 minutes after the liquid temperature had reached 200-205°. The end of the reaction was indicated by the cessation of distillation and the drop of the vapor temperature. The maximum vapor temperature was 160°. The high vapor temperature was due to the absence of rectification. The distillate totaled 14.63 g; it consisted mainly of phosphorus oxychloride, though it also contained some benzonitrile and o-toluene sulfochloride. The phosphorus oxychloride was recovered by redistilling the distillate with a 100-mm herringbone dephlegmator. Double redistillation yielded 12.2 g of phosphorus oxychloride, with a b.p. of 106-108°. and a m.p. of 1.1°, which exhibited no depression of the mixed melting point with known phosphorus oxychloride. The distillation residue was combined with the crude benzonitrile (see below). The bulk of the reaction mass was a light-brown liquid, with the unpleasant odor of the sulfochloride and benzonitrile. The reaction products were separated by distilling the mixture at 5 mm into a herringbone column 70 mm long. The crude benzonitrile distilled at 70-80°, and the o-toluene sulfochloride at 120-123°, its yield being 16.73 g, or 87.8% of the theoretical. The o-toluene sulfochloride was identified by conversion into o-toluenesulfonamide, m.p. 160-161°, exhibiting no depression of the mixed melting point with o-toluenesulfonamide.

The crude benzonitrile was mixed with the residue of the phosphorus oxychloride distillation and dissolved in 25 ml of petroleum ether (b.p. 60-70°), and the solution was treated to gaseous ammonia to remove traces of acid chlorides. One hour later the precipitate was suction-filtered and discarded, the petroleum ether being driven out of the filtrate, and the benzonitrile distilled into a 100-mm herringbone dephlegmator. The yield of the product with a b.p. of 189-190° was 8.3 g or 80.5% of the theoretical; its m.p. was -14°, not exhibiting any depression of the mixed melting point with known benzonitrile.

Preparation of p-nitrobenzonitrile from p-nitrobenzoyl chloride and recovery of benzenesulfonamide. A mixture of 0.05 mole of p-nitrobenzoyl chloride (9.28 g) and 0.05 mole of phenyl trichlorophosphazosulfone (14.63 g) was heated under the conditions set forth above. The reaction set in at 205° and was complete within 30 minutes at 215-200°. The maximum vapor temperature was 145°. This yielded 7.23 g of a lemon-yellow distillate (94.5% of the theoretical). When the distillate was redistilled, all the colored portion passed over with the first three or four drops. The bulk of the distillate consisted of phosphorus oxychloride (6.52 g, or 85.6% of the theoretical), with a b.p. of 105-107° and a m.p. of 1.1°.

The bulk of the reaction product was a red-brown liquid, which crystallized into a solid radiant mass upon cooling. The mass was ground to a powder and slowly poured into 50 ml of a 10% ammonia solution, with chilling and thorough stirring. The mixture was stirred for 10-15 minutes and set aside to stand overnight. The finely crystalline, dirty-yellow precipitate was suction-filtered, washed with water, and treated on the filter four times with 15 ml of a 10% solution of potassium hydroxide, after which it was rewashed with water. The customary treatment of the solution yielded 6.5 g of benzenesulfonamide, or 82.7% of the theoretical, m.p. 154-155°, which exhibited no depression of the mixed melting point with known benzenesulfonamide.

The yield of crude p-nitrobenzonitrile was 6.72 g, or 90.7% of the theoretical; recrystallization from water yielded colorless flat needles with a m.p. of 146-147°, which exhibited no depression of the mixed melting point with known p-nitrobenzonitrile.

Preparation of m-nitrobenzonitrile from m-nitrobenzoic acid and recovery of p-toluenesulfonamide. 0.1 mole of m-nitrobenzoic acid (16.71 g) was mixed with 0.15 mole of thionyl chloride (10.65 ml), and the mixture was refluxed on a boiling water bath. The evolution of hydrogen chloride ceased within an hour. The reflux condenser was replaced by a straight condenser, and the excess thionyl chloride was driven off up to a temperature of 150° in the liquid. The liquid was cooled to 40°, 0.1 mole of p-tolyl trichlorophosphazosulfone (30.65 g) was added, and the mixture was heated on an air bath as set forth above. The reaction set in at 185° and took 30 minutes at 208°. The maximum vapor temperature was 135°. The distillate totaled 14.9 g; it yielded 14.2 g, or 92.6% of the theoretical, of pure phosphorus oxychloride.

The principal reaction product cools into a solid, extremely hard, crystalline mass. It was therefore necessary to stir the reaction product very energetically during cooling to secure it as a fine powder. This powder was gradually added to 100 ml of 15% ammonia, chilled with ice water. The next day the crystalline precipitate was suction-filtered, washed with water, and treated on the filter with four 25 ml batches of a 10% solution of potassium hydroxide. The filtrate was boiled with activated charcoal and filtered, and the p-toluenesulfonamide was precipitated in the usual manner. The yield was 13.5 g, or 85.9% of the theoretical, with a m.p. of 135-136°. The yield of the crude m-nitrobenzonitrile was 12.3 g, or 83.0% of the theoretical; thin matted needles with a m.p. of 116-117° after recrystallization from water, which exhibited no depression of the mixed melting point with known m-nitrobenzonitrile.

Preparation of p-chlorobenzonitrile from p-chlorobenzoic acid and recovery of o-toluenesulfonamide. A mixture of 0.05 mole of p-chlorobenzoic acid (7.82 g) and 0.075 mole of thionyl chloride (5.35 ml) was refluxed for 2 hours on a boiling water bath. The excess thionyl chloride was then driven off at a liquid temperature of 150°, 0.05 mole of o-tolyl trichlorophosphazosulfone (15.33 g) was added, and the reaction was carried out as set forth above. The reaction set in at 175°, and was completed within 25 minutes at 208-215°. The maximum vapor temperature was 165°. The yield of pure phosphorus oxychloride with a m.p. of 1.1° was 6.9 g, or 90.0% of the theoretical. The yield of o-toluenesulfonamide was 6.8 g, or 86.7% of the theoretical, and the yield of p-chlorobenzonitrile was 5.85 g, or 85.2% of the theoretical. Sublimation of the nitrile at 95° and 5 mm yielded snow-white prisms with a faint pleasant fragrance and a m.p. of 92-93°, which exhibited no depression of the mixed melting point with the known p-chlorobenzonitrile.

The ortho, para, and meta tolunitriles, the ortho and para bromobenzonitriles, and phthalodinitrile were prepared in a similar manner.

SUMMARY

The mechanism involved in the conversion of trichlorophosphazosulfone-p-benzoyl chloride into p-benzonitrilesulfonyl chloride is discussed, and a new method of converting carboxylic acid chlorides into nitriles is proposed, based upon this discussion.

The procedure required for converting carboxylic acid chlorides into nitriles by the action of aryl-trichlorophosphazosufones has been worked out and checked by way of several examples.

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2) See Consultants Bureau English translation, p. 101

3) See Consultants Bureau English translation, p. 335.

SYNTHESIS OF AMINOSULFIDES AND AMINOSULFONES

VIII. SYNTHESIS OF AMINOARYL β-KETOSULFONES AND THEIR DERIVATIVES

I. Kh. Feldman and E.S.Nikitskaya

In our preceding report [1] we described the method of preparation and the properties of several sulfones in which the sulfanilyl group $NH_2C_6H_4SO_2$ was attached to a dialkyl-aminoalkyl group. The present paper deals with the synthesis and the properties of some sulfones in which an aryl or aminoaryl ketone group is attached to the sulfanilyl radical. The β-ketosulfones of the $NH_2C_6H_4SO_2CH_2COR$ type, in which $R=C_6H_5$ or $C_6H_4NHCOCH_3$, are chemically interesting because the acid nature of their methylene group enables us to replace the active hydrogen atoms in that group by various radicals, thus producing new compounds. From the standpoint of chemotherapy they are of interest in the study of the following problem: does the chemical analogy between the β-diketones and the β-ketosulfones carry over into chemotherapy?

In the literature the β-ketosulfones are usually synthesized by condensing sulfonic acids with halogen ketones [2]. They can also be prepared by oxidizing β-ketosulfides [3], which are produced in turn by condensing halogen ketones with alkali salts of thiols. In the present research, p-acetylaminophenylphenacyl sulfone was produced by condensing the sodium salt of p-acetylaminobenzene sulfinic acid with bromoacetophenone in toluene containing copper powder:

$$CH_3CONHC_6H_4SO_2Na + BrCH_2COC_6H_5 \xrightarrow{Cu} CH_3CONHC_6H_4SO_2CH_2COC_6H_5 + HBr \qquad (I)$$

The acetyl group was hydrolyzed by a mixture of hydrochloric and acetic acids; this yielded the amine hydrochloride as colorless crystals. It is worthy of note that the hydrogen chloride group is held so loosely in this product that when the latter is crystallized from alcohol, hydrogen chloride is split out, the free amine being produced as a colorless substance.

Goldberg and Besly [4], who synthesized this compound before us, hydrolyzed the acetyl group with hydrochloric acid (10 N) in isopropyl alcohol. They secured the hydrochloride as well as the free base in the form of yellow, rather than colorless, crystalline precipitates, whose melting points agree with those of the products we have synthesized. We endeavored to effect hydrolysis under the conditions specified by these authors, but here, too, we secured colorless substances.

In addition to the p-aminophenylphenacyl sulfone, we synthesized p-aminophenyl-p-aminophenacyl sulfone by reacting an alkali salt of p-acetylaminobenzenesulfinic acid with p-acetylaminochloracetophenone, followed by hydrolyzing the acetyl groups.

$$CH_3CONHC_6H_4SO_2Na + ClCH_2COC_6H_4NHCOCH_3 \rightarrow$$

$$\rightarrow \underset{(II)}{CH_3CONHC_6H_4SO_2CH_2COC_6H_4NHCOCH_3} \rightarrow$$

$$\rightarrow \underset{(III)}{NH_2C_6H_4SO_2CH_2COC_6H_4NH_2}$$

In contrast to the reaction involved in synthesizing p-acetylaminophenylphenacyl sulfone, the condensation of the sodium salt of p-acetylaminobenzenesulfinic acid and p-acetylaminochloracetophenone takes place smoothly, without the addition of copper powder. Here, too, the acetyl groups were saponified by a mixture of hydrochloric and acetic acids, while the diamine dihydrochloride formed as the result of saponi-

fication lost hydrogen chloride during crystallization.

Schiff bases were produced by condensing free amines with salicylaldehyde.

Otto [5] and Rössing [6] were the first to undertake a study of the properties of the hydrogen atoms in the methylene group alongside the sulfone group. In their researches on sulfonocarboxylic acids, they found that these acids behaved chemically like keto acids: both of these acids were decomposed by alkalies, giving off CO_2 and forming a ketone in the case of the keto acid and a sulfone in the case of a sulfono-carboxylic acid. After Otto and Rossing, several authors [7] investigated the properties of ketosulfones and disulfones, especially their influence upon an adjacent methylene group, as in the diketones.

We thought it would be interesting to investigate the reactivity of the hydrogen atoms in the methylene groups of the beta ketosulfones we had synthesized and to ascertain how the acetamino groups in the benzene rings affected their properties. With this in mind we ran experiments on the condensation of β-ketosulfones with dialkylaminoalkyl chlorides and salicylaldehyde.

The condensation of o-acetylaminophenylphenacyl sulfone with β-diethylaminoethyl chloride has been described in the literature, though the author did not isolate the condensation product in the pure state. We condensed p-acetylaminophenylphenacyl sulfone with diethylaminopropyl chloride and isolated the condensation product in the pure state. This substance is extremely hygroscopic; its analysis for nitrogen indicated, however, that we had secured the product desired. This compound was exposed to the action of an aqueous-alcoholic alkali, resulting in its cleavage together with the hydrolysis of the acetyl group; we secured a red, oily liquid, which combined with an alcoholic solution of hydrogen chloride to form an extremely hygroscopic salt, which is apparently responsible for the unsatisfactory analysis results, which are, nevertheless, close to the values computed for the dihydrochloride of p-aminophenyl-δ-diethyl-aminobutyl sulfone:

$$CH_3CONHC_6H_4SO_2CH_2COC_6H_5 + ClCH_2CH_2CH_2N(C_2H_5)_2 \xrightarrow{C_2H_5ONa}$$

$$\rightarrow CH_3CONHC_6H_4SO_2\underset{\displaystyle CH_2CH_2CH_2N(C_2H_5)_2}{\underset{|}{C}HCOC_6H_5} \xrightarrow{NaOH}$$

(IV)

$$\rightarrow NH_2C_6H_4SO_2CH_2CH_2CH_2CH_2N(C_2H_5)_2$$

(V)

When we tried to perform an analogous condensation with the other β-ketosulfone we had synthesized, p-acetylaminophenyl-p'-acetylaminophenacyl sulfone, we found that no condensation takes place under these conditions, and we recovered the initial β-ketosulfone unchanged. The second acetamino group in the para position to the carboxylic group evidently affects the reaction in this case.

It is stated in the literature that the hydrogen atoms in an acid methylene group, as in aryl sulfonoacetonitriles, react readily together, though they do not react individually. That is why they condense fairly easily with aldehydes, producing ethylenic derivatives. We condensed both of our ketosulfones with salicylaldehyde, securing the corresponding double-bond compounds; hence, the second acetamino group in p-acetylaminophenyl-p'-acetylaminophenacyl sulfone does not affect its condensation with aldehydes. Condensation was effected in pyridine to which a few drops of piperidine had been added as a catalyst.

$$CH_3CONHC_6H_4SO_2CH_2COR + CHOC_6H_4OH\text{-}o \xrightarrow[\text{pyridine}]{\text{piperidine}}$$

$$\rightarrow CH_3CONHC_6H_4SO_2CCOR \quad R = C_6H_5,\ C_6H_4NHCOCH_3$$
$$\qquad\qquad\qquad\quad \| \qquad\qquad\qquad\

Schiff base of p-aminophenylphenacyl sulfone (I) and salicylaldehyde. The Schiff base of p-aminophenylphenacyl sulfone and salicylaldehyde was produced under the same conditions as those employed for preparing the Schiff base of p-aminophenyl-p'-aminophenacyl sulfone. The yield of the base was 84%; its m.p. was 150-155°. After it had been crystallized from ethyl alcohol, the Schiff base of p-aminophenylphenacyl sulfone was a yellow crystalline substance with a m.p. of 159-161°, soluble when heated in most of the usual organic solvents, insoluble in water or dilute alcohols, and decomposed by hydrochloric acid.

Found %: N 3.79; S 8.12. $C_{21}H_{17}O_4NS$. Calculated %: N 3.69; S 8.44.

p-Acetylaminophenyl-δ-diethylaminobutyl-1-(benzoyl) sulfone (IV). 25 ml of absolute alcohol were placed in a three-necked flask fitted with a stirrer, a reflux condenser, and a dropping funnel, and 0.23 g (0.01 mole) of metallic sodium was added in small pieces. When all the sodium had dissolved, 3.17 g (0.01 mole) of p-acetylaminophenylphenacyl sulfone were added, and the reaction mixture was boiled until the ketosulfone had dissolved (30 minutes). Then 4.5 g (0.03 mole) of β-diethylaminopropyl chloride were added to the hot solution from the dropping funnel. The reaction mass was stirred and heated to 40° for 2 hours, and to the boiling point of the solution for 6 hours. When the reaction was over, the sodium chloride was filtered out, and the filtrate evaporated to small volume and poured out into water. A thick, light-brown mass settled out. It was filtered out of the water, washed, and dried in a vacuum desiccator. The 3.45 g (80% yield) of the condensation product thus secured was a dark-yellow substance that deliquesced in air, was freely soluble in the usual organic solvents, and was insoluble in water.

Found %: N 6.66, 6.79. $C_{23}H_{30}O_4N_2S$. Calculated %: N 6.51.

Dihydrochloride of p-aminophenyl-δ-diethylaminobutyl sulfone (V). A mixture of 3.45 g of p-acetylaminophenyl-δ-diethylaminobutyl-1-(benzoyl) sulfone, 20 ml of alcohol, and 20 ml of 5N sodium hydroxide was heated for two hours on a boiling water bath in a round-bottomed flask fitted with a reflux condenser. The resulting solution was neutralized with hydrochloric acid, and the alcohol driven off in vacuo. Then the cooled mass was treated with a 10N solution of sodium hydroxide until its reaction with phenolphthalein was alkaline, and the oily substance that settled out was extracted with ether. After the ether extract had been desiccated and the ether driven off, there remained in the flask the hypothetical p-aminophenyl-δ-diethylaminobutyl sulfone as 2.13 g of a tacky, noncrystallizing, dark-red mass (93% yield). It was freely soluble in the usual organic solvents and in water. Reacting an ether solution of p-aminophenyl-δ-diethylaminobutyl sulfone with an alcoholic solution of hydrogen chloride yielded the colorless, extremely hygroscopic dihydrochloride, which was refined by redissolving it in absolute alcohol and precipitating it with absolute ether.

Found %: N 7.20; Cl 18.95. $C_{14}H_{28}O_2N_2SCl_2$. Calculated %: N 7.84; Cl 19.81.

2-p-Acetylaminophenylsulfonyl-2-(benzoyl)-1-o-hydroxyphenylethylene (VI, R = C_6H_5). 100 ml of pyridine, 3.17 g (0.01 mole) of p-acetylaminophenylphenacyl sulfone, 1.5 g (0.012 mole) of salicylaldehyde, and a few drops of piperidine were placed in a three-necked flask fitted with a stirrer and a reflux condenser. As soon as the piperidine was added, the initially colorless solution turned orange. The reaction mass was then refluxed for 7 hours at a bath temperature of 100°, after which it was evaporated in vacuo to small volume, the residual thick, dark-brown mass being rubbed in a mortar with a mixture of diethyl and petroleum ethers until it turned into a sandy-yellow powder. The powder was filtered out and dried in a vacuum desiccator. The resultant condensation product weighed 3.8 g (90% yield). M.p. 70-72°. The substance was refined by dissolving it in acetic acid

and precipitating it with a mixture of petroleum and diethyl ethers. The resulting 2-p-acetylaminophenylsulfonyl-2-(benzoyl)-1-o-hydroxyphenylethylene was a light-yellow substance that fused with decomposition at 75-77°, was freely soluble in alcohols, acetone, ethyl acetate, and acetic acid, slightly soluble in benzene and ligroin, and insoluble in diethyl ether, petroleum ether, or water.

Found %: N 3.46; S 7.30. $C_{23}H_{19}O_5$ NS. Calculated %: N 3.32; S 7.60.

2-p-Acetylaminophenylsulfonyl-2-(benzoyl)-1-o-hydroxy-m,m-dibromophenylethylene (VII, R = C_6H_5).

Experiment 1. 1.05 grams (0.0025 mole) of 2-p-acetylaminophenylsulfonyl-2-(benzoyl)-1-o-hydroxyphenylethylene were dissolved in 7 ml of glacial acetic acid in a flat-bottomed flask fitted with a stopper bearing a calcium chloride tube and a dropping funnel. The contents of the flask were chilled, and a solution of 0.44 g (0.00275 mole) of bromine in 5 ml of glacial acetic acid was added. A brown mass was produced, from which the slightly oily, yellowish dibromide was isolated by adding water, the dibromide crystallizing completely when rubbed in a mortar. Then it was pressed out, washed with water until all the odor of acetic acid was removed, and dried in a vacuum desiccator. When we tried to crystallize the dibromide from dichloroethane or benzene, it dissolved, but as heating was continued, it settled out of the solution as a snow-white crystalline precipitate, the solution turning yellow. The substance was filtered out and dried in a vacuum desiccator. It weighed 1.2 g (82% yield), m.p. 223-225° (with decomp.). The dibromide dissolves when heated in glacial acetic acid or alcohol. It is recovered from the acetic acid solution as a caseous colorless precipitate.

Found %: Br 27.26. $C_{23}H_{17}O_5NSBr_2$. Calculated %: Br 27.63.

Experiment 2. 100 ml of pyridine, 3.17 g (0.01 mole) of p-acetylaminophenylphenacyl sulfone, 3.36 g (0.012 mole) of dibromosalicylaldehyde, and a few drops of piperidine were placed in a three-necked flask fitted with a stirrer and a reflux condenser. The solution turned orange. The reaction mass was refluxed for 7 hours, with stirring, at a bath temperature of 100°. Then it was poured a drop at a time into 2500 ml of 2% hydrochloric acid. The flocculent yellow precipitate was filtered out, washed with water, and dried. It weighed 4.4 g (76% yield). After it was dissolved in dichloroethane, a light cream-colored precipitate with a m.p. of 222-224° (with decomp.) settled out; the mixed melting point of which with the dibromide produced in Experiment 1 exhibited no depression.

2-p-Aminophenylsulfonyl-2-(benzoyl)-1-o-hydroxphenylethylene (VIII, R C_6H_5). 1 gram of 2-p-acetylaminophenyl-2-(benzoyl)-1-o-hydroxyphenylethylene was dissolved in 12 ml of glacial acetic acid within a round-bottom flask fitted with a reflux condenser, and 4 ml of dilute hydrochloric acid (1:1) were added to the solution. The flask's contents were refluxed for 6 hours on a water bath, turning dark red. After the 6 hours had elapsed, activated charcoal was added to the flask, and the mixture was heated for another 30 minutes. Then the charcoal was filtered out, and the yellow amino product was precipitated from the filtrate with aqueous ammonia. It weighed 0.8 g (89% yield), with a m.p. of 94-102° (with decomp.). The amine was refined by chilling and agitating it for 3 hours with 100 ml of dilute hydrochloric acid (2:1). This caused the bulk of the substance to dissolve, the balance turning into a tar, yielding a brown acid-insoluble deposit. It was filtered out, the filtrate being heated with charcoal to decolorize it, and an amine was crystallized from 70% alcohol; this yielded pure 2-p-aminophenylsulfonyl-2-(benzoyl)-1-o-hydroxyphenylethylene as a colorless crystalline substance with a m.p. of 98-100° (with decomp.). It was freely soluble in acetic acid, acetone, and alcohol, insoluble in ether, petroleum ether or ligroin, and slightly soluble in weak hydrochloric acid; strong hydrochloric acid converted it into a tar, yielding a brown deposit with an indeterminate melting point.

Found %: N 3.90; S 8.20. $C_{21}H_{17}O_4NS$. Calculated %: N 3.69; S 8.44.

2-p-Acetylaminophenylsulfonyl-(p'-acetylaminobenzoyl)-1-o-hydroxyphenylethylene (VI, R = $C_6H_5NHCOCH_3$). 100 ml of pyridine, 3.74 g (0.01 mole) of p-acetylaminophenyl-p'-acetylaminophenacyl sulfone, 1.5 g (0.012 mole) of salicylaldehyde, and a few drops of piperidine were placed in a three-necked flask fitted with a stirrer and a reflux condenser. The reaction mass was stirred and refluxed for 7 hours (100° bath temperature), the deposit of p-acetylaminophenyl-p'-acetylaminophenacyl sulfone gradually dissolving. When all of the deposit had dissolved, the reaction was complete. The solution was evaporated in vacuo to small volume, the thick, dark-brown, tarry residue being rubbed in a mortar with ether. The resultant, sand-colored powder was filtered out, washed with ether, and dried in a vacuum desiccator. It weighed 4 g (83% yield); m.p. 98-102°. The substance was purified by dissolving it in acetic acid, agitating the solution with charcoal, filtering out the latter, and using ether to precipitate the 2-p-acetylaminophenylsulfonyl-2-(p'-acetylaminobenzoyl)-1-o-hydroxyphenylethylene as a light-yellow deposit that had a m.p. of 104-106° (with decomp.). The substance was freely soluble in ethyl acetate, alcohol, acetone, acetic acid, and pyridine, and insoluble even when heated in benzene, ligroin, ether, petroleum ether, or water.

Found %: N 5.76; S 6.55. $C_{25}H_{22}O_6N_2S$. Calculated %: N 5.86; S 6.69.

2-p-Acetylaminophenylsulfonyl-2-(p'-acetylaminobenzoyl)-1-o-hydroxy-m,m-dibromophenylethylene (VII, R = $C_6H_4NHCOCH_3$).

Experiment 1. 1.2 grams (0.0025 mole) of 2-p-acetylaminophenylsulfonyl-2-(p'-acetylaminobenzoyl)-1-o-hydroxyphenylethylene were dissolved in 7 ml of glacial acetic acid in a flat-bottomed flask closed with a rubber stopper bearing a calcium chloride tube and a dropping funnel. The contents of the flask were chilled, and a solution of 0.44 g (0.00275 mole) of bromine in 5 ml of glacial acetic acid was added to it from a dropping funnel, throwing down a caseous white precipitate of the dibromide. The latter was filtered out, washed with water until the odor of acetic acid had disappeared, and dried in a vacuum desiccator. This yielded 0.96 g (60% yield) of the dibromide as a colorless precipitate with a m.p. of 110-113° (with decomp.), which yellowed upon standing. After crystallization from dichloroethane (70 ml), it was a colorless substance that was soluble in alcohols, acetone, and acetic acid, and insoluble in water, benzene, ligroin, or petroleum ether. M.p. 115-117° (with decomp.).

Found %: Br 24.75. $C_{25}H_{20}O_6N_2SBr_2$. Calculated %: Br 25.15.

Experiment 2. 100 ml of pyridine, 3.74 g (0.01 mole) of p-acetylaminophenyl-p'-acetylaminophenacyl sulfone, 3.36 g (0.012 mole) of dibromosalicylaldehyde, and a few drops of piperidine were placed in a round-bottomed flask fitted with a stirrer and a reflux condenser; the solution turned orange. The reaction mass was then stirred and refluxed for 7 hours at a bath temperature of 100°, and poured out, a drop at a time, into 2500 ml of 2% hydrochloric acid. The flocculent yellow precipitate was filtered out, washed with water, and dried. It weighed 5.4 g (84% yield). The substance had a m.p. of 115-117° (with decomp.) after crystallization from dichloroethane, and its mixed melting point with the dibromide produced in Experiment 1 exhibited no depression.

2-p-Aminophenylsulfonyl-2-(p'-aminobenzoyl)-1-o-hydroxyphenylethylene (VIII, R = $C_6H_4NH_2$). A mixture of 1 g of 2-p-acetylaminophenylsulfonyl-2-(p'-acetylaminobenzoyl)-1-o-hydroxyphenylethylene, 12 ml of glacial acetic acid, and 4 ml of dilute hydrochloric acid (1:1) was refluxed for 2 hours in a

round-bottomed flask at a bath temperature of 85-90°. Toward the end of the reaction a red-brown solution was produced. The solution was cooled and treated with aqueous ammonia until its reaction was alkaline with phenolphthalein. The amino compound was thrown down as 0.75 g (91% yield) of a yellow precipitate with a m.p. of 119-122° (with decomp.). The substance was purified by dissolving it in hydrochloric acid and reprecipitating it from the solution with aqueous ammonia. The resulting 2-p-aminophenylsulfonyl-2-(p'-aminobenzoyl)-1-p-hydroxyphenylethylene was a light-yellow substance with a m.p. of 124-126° (with decomp.), soluble in alcohol, acetone, acetic acid, and hydrochloric acid, and insoluble in benzene, ether, or ligroin.

Found %: N 6.81; S 8.13. $C_{21}H_{18}O_4N_2S$. Calculated %: N 7.10; S 8.12.

SUMMARY

1. 12 aminoaryl β-ketosulfones and their derivatives hitherto not described in the literature have been synthesized.

2. The acidic properties of the methylene groups in two β-ketosulfones—p-acetylaminophenylphenacyl sulfone and p-acetylaminophenyl-p'-acetylaminophenacyl sulfone—have been investigated, and it has been found that:

a) The hydrogen atoms of the methylene group in p-acetylaminophenylphenacyl sulfone react both with alkyl halides, yielding monoalkyl substitution derivatives, and aldehydes, yielding ethylene derivatives;

b) The hydrogen atoms of the methylene group in p-acetylaminophenyl-p'-acetylaminophenacyl sulfone do not yield a condensation product when the sulfone is reacted with alkyl halides under the conditions employed for the p-acetylaminophenylphenacyl sulfone, but when it is reacted with aldehydes they yield ethylene derivatives, as in the case of p-acetylaminophenylphenacyl sulfone;

c) The ethylene derivatives produced by reacting p-acetylaminophenylphenacyl sulfone and p-acetylaminophenyl-p'-acetylaminophenacyl sulfone with salicylaldehyde react with bromine, yielding dibromides; the bromine is not added at the double bond, however, but enters the ring of the salicylaldehyde group;

d) Hydrolyzing the acetyl groups in the resulting ethylene derivatives yields amino compounds whose double bond cannot be hydrogenated at standard pressure and room temperature by Raney's nickel catalyst or by Adams' platinum catalyst.

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SYNTHESIS OF AMINOSULFIDES AND AMINOSULFONES

IX. A NEW TYPE OF DIAMINOSULFONES

I. Kh. Feldman and A. E. Gavrilova

The drugs known as sulfanilamides (streptocide, sulfidine, sulfazole, etc.) have played a major role in the history of the development of chemotherapy in general and in the chemotherapy of infectious diseases in particular. It is hard to exaggerate the importance of this group of drugs in medical practice and veterinary medicine in the treatment of coccus and other infections of man and animals. We know that antibacterial activity is a property in some degree or another of sulfanilamides with the structure of $NH_2C_6H_4SO_2R$, where R is an ammonia residue or an organic amine. At the beginning of World War II Domagk and others [1] synthesized a new preparation called "marphanil" with the structure of $NH_2CH_2C_6H_4SO_2NH_2$, which differed from sulfanilamide (white streptocide) only in having a benzyl radical instead of a phenyl radical, so that this series of compounds could be called homosulfonamides. According to the literature, marphanil proved to be especially active against the organism causing gas gangrene.

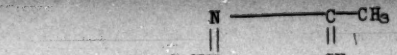
The greatest interest attaches to the fact that paraaminobenzoic acid, which is an antagonist of sulfanilamide and its derivatives, exerts no retarding effect upon the action of marphanil on microbes. We were interested in the chemical behavior and the antibacterial properties of a series of compounds in which the methylene group would not be located between the phenyl radical and the aromatic amine as in marphanil, $NH_2CH_2C_6H_4SO_2NH_2$, but between the sulfonyl group and the aliphatic amine, $NH_2C_6H_4SO_2CH_2NH_2$. Compounds of this sort are true sulfones, even though they contain an SO_2 group and an amine residue, since the SO_2 group is located between two carbon atoms.

To secure compounds of this type we started out with p-acetaminophenylsulfinic acid, which was prepared by the method referred to in the literature [2]. We found that it readily added one molecule of formaldehyde in alcohol, yielding p-acetylaminophenylmethylol sulfone (I). The hydroxyl group in this compound is highly active, reacting readily with ammonia, and with primary and secondary amines to yield sulfones of varying degrees of stability to acids or alkalies.

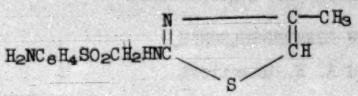
$$CH_3CONHC_6H_4SO_2H + H_2CO \longrightarrow CH_3COHNC_6H_4SO_2CH_2OH, \quad (I)$$

The p-acetaminophenyl methylol sulfone (methylol) undergoes no change when dissolved in hot water; when heated with acids or alkalies, it breaks down, while the methylol reacts with acetic anhydride to yield the acetic ester $CH_3COHNC_6H_4SO_2CH_2OCOCH_3$ (II).

When the methylol is condensed with aniline in absolute alcohol, we get the corresponding amine, $CH_3COHNC_6H_4SO_2CH_2NHC_6H_5$ (III), one molecule of water being evolved. This compound resists the action of dilute acids and alkalies fairly well. When it is heated with 1:1 hydrochloric acid, the acetyl group is hydrolyzed, yielding the free amine, $H_2NC_6H_4SO_2CH_2HNC_6H_5$ (IV). The condensation product of methylol and 2-amino-4-methylthiazole (V) has approximately the same properties. When the resultant 4-acetaminophenyl (2'-amino-4'-methylthiazolyl) methane sulfone is hydrolyzed with dilute (1:1) hydrochloric acid, we get the free amine (VI):

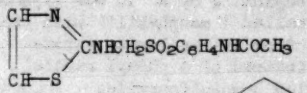


(V)

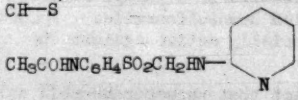


(VI)

On the other hand, the condensation products of methylol and 2-aminothiazole (VII), 2-aminopyridine (VIII), and ammonia (IX) are unstable in the presence of dilute acids and alkalies. All endeavors to hydrolyze the acetyl group in these compounds resulted in a mixture of substances. Either the initial products or p-acetaminophenylsulfinic acid can be isolated from the reaction products, depending upon the acid employed (hydrochloric or acetic), its concentration, and the temperature at which hydrolysis is performed.



(VII)



(VIII)

$CH_3COHNC_6H_4SO_2CH_2NH_2$ (IX)

When the condensation product of methylol and the diethylamine p-acetaminophenyl (diethylamino) methane sulfone $CH_3COHNC_6H_4SO_2CH_2N(C_2H_5)_2$ (X) is hydrolyzed with dilute hydrochloric acid, we can isolate a small quantity of the free amine $H_2NC_6H_4SO_2CH_2N(C_2H_5)_2$ (XI).

EXPERIMENTAL

p-Acetaminophenylsulfonylmethylol (I). 30 grams (0.15 mole) of p-acetaminophenylsulfinic acid and 150 ml of absolute ethyl alcohol heated to 60° were placed in a round-bottomed flask fitted with a reflux condenser and a mechanical stirrer, and the mixture was stirred while 18 g (0.24 mole) of 40% formaldehyde were added. At first a solution was produced, from which a white precipitate soon settled out. The reaction mass was heated to 50-60° for an hour; when it had cooled, the precipitate was filtered out and dried in a vacuum desiccator. M.p. 163-164°; weight 31 g (89.9% of the theoretical). The substance crystallized from ethyl alcohol as lamellae with a m.p. of 161-162°. It was soluble in hot water, alcohol, and acetone, and insoluble in ether, benzene, or chloroform.

Found %: N 5.93; S 13.99. $C_9H_{11}O_4NS$. Calculated %: N 6.11; S 13.97.

Acetic ester of p-acetaminophenylsulfonylmethylol (II). 10 grams of p-acetaminophenylsulfonylmethylol were heated to 85-90° for three hours with 50 ml of acetic anhydride in a round-bottomed flask fitted with a reflux condenser. The reaction yielded a solution, from which a white crystalline substance settled out upon cooling; it was filtered out, washed with water, and dried. It weighed 6 g. Another 4 g of the substance, with a m.p. of 195-197 g, was secured from the filtrate by diluting it with water. The yield totaled 10 g, or 84.7% of the theoretical. The m.p. was 199° after crystallization from ethyl alcohol. The substance was insoluble in water, ether, benzene, dichloroethane, or chloroform.

Found %: S 11.81. $C_{11}H_{13}O_5NS$. Calculated %: S 11.80.

p-Acetaminophenyl anilyl methane sulfone (III). 10 grams (0.043 mole) of p-acetaminophenylsulfonylmethylol and 50 ml of absolute ethyl alcohol were placed in a round-bottomed flask fitted with a mechanical stirrer and a reflux condenser and stirred while 4.5 g (0.48 mole) of aniline were added. The mixture formed a solution when heated to 50°; the solution was heated to 70°, and after 45 minutes at that temperature a crystalline substance settled out. Heating was continued for 6 hours at 70-80°. After the mixture had cooled, the product was filtered out and washed successively with a 2% alkali solution, water, and ether. This yielded 9.5 g, or 73% of the theoretical, of dry substance with a m.p. of 187-189°. The substance's m.p. was raised to 190-191° after crystallization from 75% alcohol; it was cream-colored, turning yellow in air; it was freely soluble in acetone, dissolving when heated in ethyl alcohol, and insoluble in water, ether, benzene, or dichloroethane.

Found %: S 10.30; N 8.83. $C_{15}H_{16}O_3N_2S$. Calculated %: S 10.52; N 9.2.

p-Aminophenyl anilyl methane sulfone (IV). 4 grams of p-acetaminophenyl anilyl methane sulfone and 20 ml of dilute (1:1) hydrochloric acid were placed in a round-bottomed flask fitted with a reflux condenser and the mixture was heated to 80-90° for 2 hours. After the solution had cooled, aqueous ammonia was added, throwing down a precipitate, which was filtered out, redissolved in dilute (1:2) hydrochloric acid, and reprecipitated with aqueous ammonia. The resultant precipitate was filtered out, washed with water, and dried, yielding 3 g, or 87% of the theoretical. The m.p. of the substance was 205-206° after crystallization from ethyl alcohol. It is white, turning yellow when exposed to the air, dissolves when heated in ethyl alcohol, or acetone, and is insoluble in water, ether, chloroform, or benzene.

Found %: N 10.55. $C_{13}H_{14}N_2O_2S$. Calculated %: N 10.68.

p-Acetaminophenyl (2'-amino-4'methylthiazolyl) methane sulfone (V). 10 grams (0.043 mole) of p-acetaminophenylsulfonylmethylol and 150 ml of absolute ethyl alcohol were placed in a round-bottomed flask fitted with a mechanical stirrer and a reflux condenser and stirred while 5 g (0.043 mole) of 2-aminothiazole were added. The mixture was then heated to 70°, causing everything to dissolve, and heating was continued at this temperature for another 10 hours. The reaction resulted in the precipitation of a white crystalline substance from the solution; it was filtered out and washed successively with a 5% alkali solution, water, and ether. This yielded 10 g of dry substance, or 71% of the theoretical, with a m.p. of 210-212°. The m.p. was 212-213° after crystallization from 75% ethyl alcohol. The substance was white, dissolved in ethyl alcohol and acetic acid, and was insoluble in water, ether, benzene, or chloroform.

Found %: N 13.08; S 19.62. $C_{13}H_{15}O_3N_3S_2$. Calculated %: N 12.92; S 19.69.

p-Aminophenyl (2'-amino-4'-methylthiazolyl) methane sulfone (VI). 10 grams of p-acetaminophenyl (2'-amino-4'methylthiazolyl) methane sulfone, m.p. 212-213°, and 60 ml of dilute (1:1) hydrochloric acid were placed in a round-bottomed flask fitted with a reflux condenser, and the mixture was heated to 80-90° for 2 hours. A solution was formed, to which a 10% alkali solution was added after it had cooled. The white precipitate that was thrown down was filtered out, washed with water, and dried. It weighed 8 g (90%) and had a m.p. of 170-173°. The m.p. was 174° after crystallization from ethyl alcohol; the substance was insoluble in water, ether, benzene, or chloroform, and soluble in ethyl alcohol and acetone.

Found %: N 14.70; S 22.36. $C_{11}H_{13}O_2N_3S_2$. Calculated %: N 14.84; S 22.61.

p-Acetaminophenyl (2'-aminothiazolyl) methane sulfone (VII). 15 grams (0.065 mole) of p-acetaminophenylsulfonylmethylol, 75 ml of absolute ethyl alcohol, and 7 g (0.07 mole) of 2-aminothiazole were placed in a round-bottomed flask fitted with a mechanical stirrer and a reflux condenser and the mixture was heated to 75-80° and stirred for 8 hours. At first a solution was formed, from which a white crystalline substance settled out as heating was continued. After the reaction mixture had cooled, the substance was filtered out, washed with ether, and dried, the m.p. of the technical product being 148-150°. It weighed 13 g (65% of the theoretical yield). The m.p. rose to 150-152° after crystallization from ethyl alcohol. The substance dissolved when heated in ethyl alcohol, acetone, and water, and was insoluble in ether, benzene, chloroform, or dichloroethane.

Found %: N 13.51; S 20.47. $C_{12}H_{13}O_3N_3S_2$. Calculated %: N 13.50; S 20.57.

p-Acetaminophenyl (2'-aminopyridyl) methane sulfone (VIII). 10 grams (0.045 mole) of p-acetaminophenylsulfonylmethylol, 50 ml of absolute ethyl alcohol, and 5 g (0.05 mole) of 2-aminopyridine were placed in a round-bottomed flask fitted with a stirrer and a reflux condenser, and the mixture was stirred and heated to 70-80° for 10 hours. At first a solution formed, from which a precipitate later settled out. After the mixture had cooled, the product was filtered out and washed with ether. This yielded 8.5 g (65% of the theoretical) of a white substance that had a m.p. of 158-159° after crystallization from ethyl alcohol. It dissolved when heated in water, ethyl alcohol, and acetone and was also soluble in dilute alkali. It was insoluble in ether, benzene, or chloroform.

Found %: N 13.98; $C_{14}H_{15}O_3N_3S$. Calculated %: N 13.77.

p-Acetaminophenyl aminomethane sulfone (IX). 25 grams (0.11 mole) of p-acetaminophenylsulfonylmethylol and 100 ml of absolute ethyl alcohol were placed in a round-bottomed flask fitted with a mechanical stirrer and a reflux condenser and stirred while 15 ml (0.17 mole) of 20% aqueous ammonia was slowly added. A solution was formed at first, from which a white crystalline substance settled out gradually. The reaction mixture was stirred for three hours at room temperature, after which the precipitate was filtered out and dried; it weighed 23.5 g, or 94% of the theoretical yield, with a m.p. of 225-226°. Its m.p. was 226-227° after crystallization from 85% ethyl alcohol. The substance was freely soluble in water and dilute alkali, slightly soluble in ethyl alcohol, and insoluble in ether, acetone, benzene, or dichloroethane.

Found %: N 12.09; S 14.37. $C_9H_{12}O_3N_2S$. Calculated %: N 12.28; S 14.03.

p-Acetaminophenyl (diethylamino) methanesulfone (X). 10 g (0.043 mole) of p-acetaminophenylsulfonylmethylol, 40 ml of absolute ethyl alcohol, and 3.5 g (0.04 mole) of diethylamine were placed in a round-bottomed flask fitted with a mechanical stirrer and a reflux condenser, and the mixture was heated to 50-60°, with stirring, for 10 hours. A solution was formed; after it had cooled, acetone was added until all the reaction product had been thrown down. This yielded a white crystalline substance, which was filtered out, washed with acetone, and dried. It weighed 8.5 g, or 70% of the theoretical yield. Its m.p. was 170-171° after crystallization from ethyl alcohol. The substance was soluble in water and ethyl alcohol and insoluble in acetone, benzene, chloroform, or dichloroethane.

Found %: N 10.06; S 11.71. $C_{13}H_{20}O_3N_2S$. Calculated %: N 9.85; S 11.26.

p-Aminophenyl (diethylamino) methane sulfone (XI). 6 grams of p-acetaminophenyl (diethylamino) methane sulfone and 30 ml of 12% hydrochloric acid

were placed in a round-bottomed flask fitted with a reflux condenser, and the mixture was heated to 70-80° for 2 hours. A solution formed, and after it had cooled, aqueous ammonia was added until the reaction to litmus was alkaline. The solution was then filtered and evaporated in vacuo to small volume. Upon cooling a white substance settled out, which was filtered and crystallized from water. This yielded white crystals as needles with a m.p. of 162-163°. The substance was soluble in hot water, ethyl alcohol, and acetone and insoluble in benzene or chloroform.

Found %: N 11.47. $C_{11}H_{18}O_2N_2S$. Calculated %: N 11.57.

SUMMARY

1. Ten compounds of a new type of diamino sulfones, $RHNC_6H_4SO_2CH_2NHR'$, have been synthesized.

2. The initial product used in synthesizing this series of sulfones was p-acetaminophenyl methylol sulfone, $CH_3COHNC_6H_4SO_2CH_2OH$, whose hydroxyl group is extremely active, reacting readily with ammonia and with primary and secondary amines.

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RESEARCH ON SULFONATION

XX. SULFONATION OF SULFO ACIDS, THEIR SODIUM SALTS, AND THEIR ACID HALIDES

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The chemical literature contains several references to instances of sulfonation in which sodium salts of sulfo acids are used instead of the free sulfo acids in order to investigate the relative velocity or degree of sulfonation of the sulfo acid used, on the assumption that the sulfo acids and their sodium salts are sulfonated at the same rate [1, 7]. The results of these experiments cannot be considered irreproachable, since there are references in the literature to the catalytic action of salts of sodium and other metals in sulfonation. Behrend and Mertelsmann [2], for example, found, in their investigation of the rearrangement of meta and para disulfo acids, that the sodium salts of these acids are sulfonated converting benzene into a 1,3,5-trisulfonic acid, whereas the free acids are not sulfonated under the same conditions. Ambler and Cotton [3] believe that the presence of sodium or potassium sulfate in the sulfuration mixture increases the amount of benzene sulfonated per minute. This catalytic action is not very intense, however. Geizer and Korovitskaya [4] also noticed a certain acceleration of sulfonation by alkali metals when added as sulfates. Lauer and Hirata [5] do not regard the acclerating action of potassium sulfate upon the sulfonation of anthraquinone by sulfuric acid as catalytic, since the reaction velocity returns to nearly the initial value before any additive is added when the amount of bisulfate is increased; moreover, the reaction is retarded in oleum.

According to V. V. Kozlov's experiments [6], nearly twice as much chlorosulfonic acid is required to produce anthraquinone β-sulfochloride when sodium sulfate is present.

Research on the process involved in the introduction of a second or third sulfo group during sulfonation or on the isomerization of sulfo acids is complicated by the difficulties arising in the production of anhydrous sulfo acids, which has compelled some authors to employ sodium salts or salts of other metals instead of the acids in such cases [1,7]. In our investigations we, too, have encountered difficulties of this sort. We thought that the sodium salts could not be employed instead of the free sulfo acids in studying the absolute or relative velocities of sulfonation, desulfonation, or isomerization without appropriate tests. This led us to undertake the present research, in order to ascertain whether sulfonation of free sulfo acids, their sodium salts, and their acid halides yielded the same results, all other conditions being equal.

Dehydrated β-naphthalenesulfonic acid and p-toluenesulfonic acid, as well as their sodium salts and halides, were sulfonated with sulfuric acid or chlorosulfonic acid. The p-toluenesulfonic acid was likewise sulfonated with anhydrous sodium sulfate present.

Sulfonation with sulfuric acid. The experiments on the relative sulfonation rate were run by heating the substance to be sulfonated to 100° in sealed tubes together with sulfuric acid. The chlorides were sulfonated in tubes that were closed by a stopper with a Bunsen valve for the free escape of hydrogen chloride. The results of our experiments on the sulfonation of β-naphthalene sulfo derivatives are listed in Table 1. From 3.5 to 5 moles of sulfuric acid were used per mole of the substance to be sulfonated in all the experiments in order to perform the reaction in a homogeneous system. The acid chloride is very poorly soluble in 92% sulfuric acid, so that a two-phase system was constituted at the beginning of sulfonation in every instance. The chloride was hydrolyzed, however, and the

reaction mass became homogeneous within 1.5 to 2.5 hours. All the hydrogen chloride was removed from the reaction zone. The test results given in Table 1 show that the acid chloride is sulfonated most readily. Hydrolysis of the chloride requires 1 mole of water as follows:

Table 1

Sulfonation of β-Naphthalenesulfonic Acid, of its Chloride, and of its Sodium Salt at 100°

Test No.	Heating time, hours	Substance Sulfonated	Sulfuric Acid: Concentration %	Sulfuric Acid: Moles used per mole of sulfo deriv.	Water: In sulfo acid, grams	Water: Added to the mixture, grams	Sulfonated in % of the substance used	% of H_2SO_4 in the mixture after heating
13	4	Acid	92.67	3.985	0.0083	—	85	86.1
14		Chloride		3.987	—	0.0088	93	90.3
15		Salt		3.988	—	0.0080	48	89.4
19	8	Acid	92.76	3.554	0.0130	—	87	85.3
20		Chloride		3.530	—	0.0124	93	89.7
21		Salt		3.554	—	0.0120	47	89.2
21a		Salt		3.616	—	—	51	88.9
7	8	Acid	92.54	5.137	—	—	91	87.5
8		Chloride		5.137	—	—	94	91.1
9		Salt		5.220	—	—	81	88.2
4	24	Acid	92.16	3.990	—	—	91	85.3
5		Chloride		3.998	—	—	95	90.1
6		Salt		3.986	—	—	77	86.5

which is why the chloride exhibits the highest percentage sulfonation. The last column in Table 1 gives the concentration of sulfuric acid in the reaction mixture, the figure being always some 4-5% higher than its concentration in the reaction mixture after sulfonation of the free sulfo acid.

As for the sulfonation of the sodium salt of the sulfo acid, its sulfonation is always much slower than that of the chloride or of the free sulfo acid, notwithstanding the fact that the concentration of sulfuric acid in the mixture is always higher than in the experiments on the sulfonation of the sulfo acid. The heterogeneity of the reaction mixture, even though temporary, cannot be the reason for the lower rate at which the sodium salt of the sulfo acid is sulfonated, since the salt dissolves in 3.5-5 moles of sulfuric acid within 10-15 minutes. The weaker dehydrating action of the sulfo acid salt than that of the free sulfo acid might be the cause. The initial sodium salt of the acid or the resultant acid salt of the disulfo acid cannot attract as much water as can be attracted by a free mono or disulfo acid, thus increasing the sulfuric acid concentration somewhat. If an exchange reaction takes place between the salt and the sulfuric acid, this lowers the concentration of the sulfuric acid, owing to the formation of a bisulfate. This conjecture is not borne out, however, as is indicated by our tests on sulfonating the sodium salt of p-toluenesulfonic acid with a single mole of sulfuric acid, as compared to the sulfonation tests of the free acid, the results being tabulated in Table 2.

Thus, more sulfuric acid was used per mole in Tests 28,35, and 41 than in the corresponding Tests 27, 34, and 40; nevertheless, the degree of sulfonation, here

Table 2

Sulfonation of p-Toluenesulfonic Acid, of its Chloride, and of its Sodium Salt at 100°.

Series No.	Test No.	Heating time, hrs	Substance Sulfonated	Sulfuric Acid: Concentration %	Sulfuric Acid: Moles used per mole of sulfo deriv.	Water: In sulfo acid, grams	Water: Added to the mixture grams	Moles added per mole of sulfo deriv.	Sulfonated in % of the substance used	% of H_2SO_4 in the mixture after heating
1	25	24	Acid	93.23	3.190	0.0096			6	92.3
	26		Chloride		3.192		0.0094		21	93.0
	27				3.191		0.0093		0	93.2
	28		Salt		4.124		0.0096		1	93.1
	29				5.054		0.0100		3	93.0
2	54	25	Acid	93.75	3.60	0.0081			15	92.2
	55				4.112	0.0114		Na_2SO_4 0.49	2	93.1
	56		Chloride		3.60	0.	0.0068		26	96.1
	58		Salt		3.58		0.0076		2	93.2
3	30	100	Acid	93.00	3.839	0.0142			19	91.6
	31				4.381	0.0100		Na_2SO_4 0.51	8	92.2
	32		Chloride		3.837		0.0146		33	94.4
	33				3.839		0.0146	Water 1.00	14	91.3
	34		Salt		3.840		0.0142		1	92.2
	35				4.841		0.0144		3	92.1
4	36	25	Acid	98.90	2.478	0.0070			20	96.8
	37				3.062	0.0078		Na_2SO_4 0.51	12	98.3
	38		Chloride		2.681		0.0076		84	99.0
	39				2.461		0.0070	Water 1.06	17	96.4
	40		Salt		2.478		0.0068		2	98.3
	41				3.468		0.0074		6	98.1

too, is much lower than in the sulfonation of the free acid (Tests 25,30, and 36). Thus, the presence of sodium as a salt retards sulfonation. This is borne out by the results of Tests 55, 31, and 37, in which the free acid was sulfonated with the addition of half a mole of anhydrous sodium sulfate and half a mole of sulfuric acid, since the sulfate converted into the bisulfate requires just as much sulfuric acid. The presence of the sodium sulfate also diminishes the sulfonation rate, though not as much as when the sodium is introduced as a sulfonate.

The p-toluenesulfonyl chloride is likewise sulfonated faster than the free acid or its sodium salt. To prove that this increase in velocity is due solely to the increase in the concentration of the sulfuric acid when the chloride is hydrolyzed, we added 1 mole of water per mole of the chloride in Tests 33 and 39,

which made the per cent sulfonation approach that for the sulfo acid (in Test 33 the per cent sulfonation was somewhat lower, since the chloride is hydrolyzed gradually, two layers being observed even two hours after the start of the run).

The foregoing experiments show that sodium greatly retards the sulfonation reaction, whether it is added as the sulfonate or the sulfate. We know that sodium bisulfate and other alkali bisulfates dissolved in sulfuric acid are conductors and lower the freezing point by 12 to 13° per mole (instead of the 6.154° per mole of a nonelectrolyte), which means that 1 mole of the salt yields two moles of solute—1 mole of sodium ions and 1 mole of bisulfate ions.

The action of sodium salts may be regarded as resembling that of water, since the reactions of water, sulfate, and sulfonate with sulfuric acid are as follows:

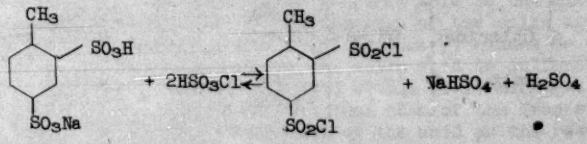
$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

$$H_2SO_4 + SO_4^{--} \rightleftharpoons 2HSO_4^-$$

$$H_2SO_4 + ArSO_3^- \rightleftharpoons HSO_4^- + ArSO_3H$$

This analogy is substantiated by the fact that just as the addition of water to strong sulfuric acid increases its acidity function, the acidity function of concentrated acid solutions is increased by the introduction of a salt. In both instances the base HSO_4^- is introduced.

Sulfonation with chlorosulfonic acid. Table 3 gives the results of our tests of sulfonating p-toluenesulfonic acid and its derivatives with chlorosulfonic acid. In the first set of experiments, the sulfo acid, its salt, and its chloride were sulfonated with 5 moles of chlorosulfonic acid, the sulfo mixture being poured over ice, and the chloride filtered out. The yield of the disulfochloride was highest when the chloride was sulfonated. The yield of the disulfochloride from the sodium salt was only 2/3 the yield secured from the free sulfo acid and half the yield secured from the chloride. Moreover, the melting point of the resultant disulfochloride indicates that a product of the highest quality is secured when the chloride is sulfonated, the quality being lowest when the salt is sulfonated. Inasmuch as the sulfochloride and the sulfo acid are in equilibrium in the medium consisting of a mixture of sulfuric and chlorosulfuric acids [8], it must be supposed that when sodium is present, the equilibrium



will have a different constant than the system in which no metal is present, this equilibrium being shifted strongly toward the formation of a salt of the sulfo acid. Thus, it is highly disadvantageous to use the sodium salt of a sulfo acid as the initial product if we wish to secure a disulfochloride by means of chlorosulfonic acid.

On the assumption that all the initial product is converted into a disulfo derivative in a reaction with chlorosulfonic acid and that the yield of the dichloride after the reaction is terminated depends solely upon the proportions of the chlorosulfonic acid, the sulfuric acid, and the sodium bisulfate, we ran a second series of tests, in which enough sulfuric acid monohydrate or sodium sulfate was introduced into the system to leave 1.5 moles of chlorosulfonic

acid, 1.5 moles of sulfuric acid, and 1 mole of the bisulfate in the system after the reaction was over in every run. The results of this series of tests (Nos. 51, 52, and 53) indicate that the dichloride yield remained nearly the same, but that the percentage of the monosulfochloride in the product secured from the salt was higher than in the other tests, to judge by the lowering of the melting point of the reaction product. This shows that here, again, the reaction is slower when the salt is sulfonated than when the chloride or the acid is sulfonated.

Table 3

Sulfonation of p-Toluenesulfonic Acid, its Chloride, and its Sodium Salt With Chlorosulfonic Acid at 100° for 3 Hours

Test No.	Substance Sulfonated	Water in Sulfo Acid, Moles	Moles used per mole of the sulfo derivative			Dichloride yield as % of the theoretical	Melting point of the dichloride produced
			HSO_3Cl	H_2SO_4	Na_2SO_4		
49	Chloride	—	4.94	—	—	84.0	50—55
48	Acid	0.08	5.19	—	—	68.8	48—52
50	Salt	—	5.08	—	—	44.5	40—48
52	Chloride	—	3.35	1.02	0.49	32.7	50—53
51	Acid	0.08	4.44	—	0.50	33.1	48—52
53	Salt	—	4.40	0.51	—	36.1	30—35

Thus, in sulfonating with chlorosulfonic acid, as was the case with sulfuric acid, the reaction is easiest with the sulfochloride, more difficult with the sulfo acid, and still more difficult with the sodium salt of the sulfo acid.

Description of Experiments

The free β-naphthalenesulfonic acid was prepared in the usual manner as a monohydrate with a molecular weight of 228 by titration with 0.1N alkali. The acid was used to prepare the salt, the latter yielding the chloride with a m.p. of 75° when treated with phosphorus pentachloride.

Technical p-toluene sulfochloride was crystallized from ether, distilled in vacuo, and recrystallized from ether, having a m.p. of 69° after this refining. The acid was prepared by saponifying the sulfochloride, the acid yielding the sodium salt.

The sulfo acids were dehydrated by heating them in test tubes to a temperature not in excess of 100° inside a vacuum desiccator over pieces of sodium hydroxide. The amount of residual water in the sulfo acid was determined from the loss of weight of each test tube. Complete dehydration required either too long heating or a higher temperature, entailing the formation of sulfones and tars in the acid, as indicated by the formation of a turbid solution when the sulfo acid is dissolved in water.

After about 1 gram of the substance to be sulfonated had been heated with the sulfuric acid, the mixture was dissolved in water, the solution diluted to make 500 ml, and 50 ml of it titrated with 0.1N alkali. The percentage of substance sulfonated was determined from the difference between the acid equivalents before and after the run. Inasmuch as the excess of sulfuric acid was frequently substantial, this difference proved to be quite small, so that the accuracy of our determinations of the percentage of disulfo acid formed did not exceed 1-2%.

The chlorosulfonic acid used was distilled once at ordinary pressure. Before use, the sodium sulfate was calcined in a crucible over a Bunsen burner.

SUMMARY

Sulfonation of β-naphthalenesulfonic acid, its sodium salt, and its chloride with sulfuric acid has shown that the chloride is sulfonated at the fastest rate, and the sodium salt most slowly, with the sulfo acid occupying an intermediate position between the two.

The same behavior pattern is found to exist in the sulfonation of p-toluenesulfonic acid, its sodium salt and its chloride. When sodium sulfate is present, the rate at which the p-toluenesulfonic acid is sulfonated likewise falls.

The chloride is sulfonated more rapidly owing to the consumption of 1 mole of water from the reaction mixture in hydrolyzing it. The sodium introduced as the sulfate or the sulfonate lowers the sulfonation rate, though increasing the acidity function of the sulfuric acid, as was the case with water.

The reaction rate is likewise lowered when a sodium sulfonate is present in sulfonation with chlorosulfonic acid. Sodium also affects the equilibrium between the sulfo acid and its chloride in the mixture of sulfuric and chlorosulfonic acids.

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THE N-ARYL AMIDES OF HYDROXY CARBOXYLIC ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

XI. THE INTRAMOLECULAR CONDENSATION OF THE ARYL AMIDES OF 4,4'-DIMETHOXYBENZILIC ACID

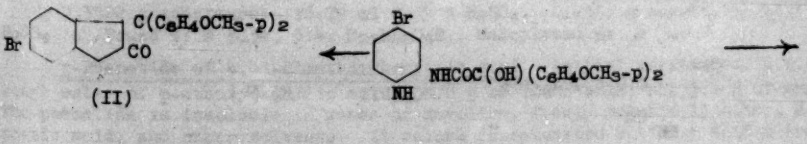
P. A. Petyunin

Introducing methoxy groups into the phenyl radicals attached to the carbinol carbon atom in aryl amides greatly increases the basic properties of the latter. This is manifested in the ability of the aryl amides to form halochromic salts with dilute mineral acids. We were therefore interested in making a study of the intramolecular condensation of the aryl amides of 4,4'-dimethoxybenzilic acid, $ArNHCOC(OH)(C_6H_4OCH_3)_2$, where Ar = C_6H_5, o-$CH_3C_6H_4$, p-$C_2H_5OC_6H_4$, m-BrC_6H_4, α-$C_{10}H_7$ or β-$C_{10}H_7$. The following condensing media were employed: concentrated sulfuric, hydrochloric, and phosphoric acids, and a 60% solution of sulfuric acid. Condensation was successful in every case. The use of various mineral acids for condensation indicates that the condensation is governed by the internal structure of the organic action of the halochromic salt (I) and is independent of the nature of the acid anion.

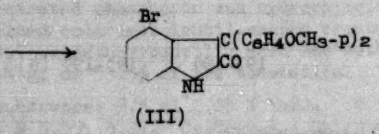
$$[ArNHCOCAr_2]^+X^-$$

(I)

In condensing the m-bromanilide of 4,4'-dimethoxybenzilic acid we might expect two isomers:



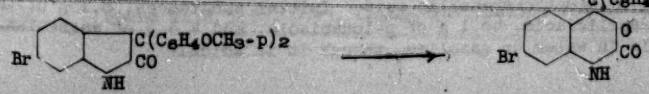
(II)



(III)

to be formed.

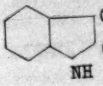
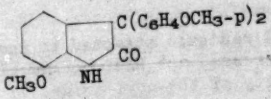
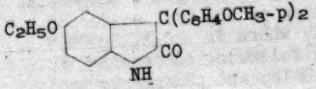
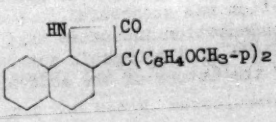
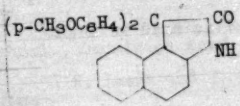
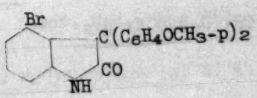
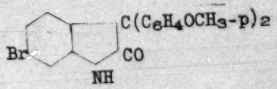
Steric hindrances make their appearance in the ortho condensation, as manifested by a sharp drop in the yield of the ortho condensation product, (III) down to 1.31%, the yield of the compound (II) being 75.6%. Both of these compounds have been described in the literature. Moreover, the structure of the para condensation product (II) has been proved by converting it into the known anhydride of 6-bromodianisoleisatoic acid (IV):



(II)

(IV)

The substances synthesized and their properties are listed in the table.

No.	Formula	Melting Point	M.p. given in the literature
1		156-157°	156-157° [3]
2		212-213	
3		179-180	
4		199-201	
5		270	
6		209-211	211 [4]
7		193-194	193-194 [4]

EXPERIMENTAL

Ethyl ester of m-bromoxanilic acid. This was prepared by heating 13 g of m-bromaniline with 17 g of ethyl oxalate. It is insoluble in water and soluble in organic solvents. It crystallizes from alcohol as colorless prisms with a m.p. of 127°. The yield was 12 g, or 69.4% of the theoretical. We are the first to have prepared the ethyl ester of m-bromoxanilic acid.

0.1572 g subs: 0.1041 g AgBr. Found %: Br 28.18. $C_{10}H_{10}O_3NBr$. Calculated %: Br 28.35.

m-Bromanilide of 4,4'-dimethoxybenzilic acid. Initial substances: 8.1 g of the ethyl ester of m-bromoxanilic acid, 46.1 g of p-iodanisole, and 4.4 g of magnesium. The anilide is insoluble in water or gasoline, though it is soluble

in ether, alcohol, acetic acid, and benzene. It colors concentrated sulfuric acid violet, the color disappearing completely upon heating or prolonged standing. It crystallizes from alcohol as colorless needles with a m.p. of 149.5°. The yield was 8.5 g, or 63.68% of the theoretical. We are the first to have produced the m-bromanilide of 4,4'-dimethoxybenzilic acid.

0.1227 g substance: 0.0520 g AgBr. 0.1387 g substance: 0.0581 g AgBr. Found %: Br 18.03, 17.82. $C_{22}H_{20}O_4NBr$. Calculated %: Br 18.08.

Anilide of 4,4'-dimethoxybenzilic acid. The following were used for the reaction: 3.3 g of ethyl oxanilate, 19.7 g of p-iodanisole, and 2.1 g of magnesium. The reaction mass was decomposed with a solution of ammonium chloride, and the reaction product extracted with ether. Driving off the solvent left behind a light-yellow oil that crystallized within 4 days. The anilide crystallized from benzene as colorless lamellae with a m.p. of 110.5-111.5°. It is insoluble in water and freely soluble in organic solvents. It colors concentrated sulfuric acid violet, the color vanishing upon prolonged standing or heating on a water bath. It colors phosphoric and hydrochloric acids crimson. The anilide of 4,4'-dimethoxybenzilic acid is not described in the literature.

0.3201 g substance: 8.3 ml 0.1 N H_2SO_4. 0.4128 g substance: 10.5 ml 0.1 N H_2SO_4. Found %: N 3.63, 3.55. $C_{22}H_{21}O_4N$. Calculated %: N 3.86.

o-Aniside of 4,4'-dimethoxybenzilic acid. The following were used for the reaction: 5.51 g of the ethyl ester of o-methoxyoxanilic acid, 34.8 g of iodanisole, and 3.6 g of magnesium. The aniside is insoluble in water or gasoline, but is soluble in the ordinary organic solvents. Crystallization from alcohol yielded colorless needles with a m.p. of 162-162.5°. It dissolves in concentrated sulfuric acid, coloring it violet, and in concentrated phosphoric and hydrochloric acids, turning them crimson. The color vanishes completely when heated or when allowed to stand at room temperature. The yield was 5 g, or 51.02% of the theoretical. The o-aniside of 4,4'-dimethoxybenzilic acid has not been described in the literature.

0.3522 g substance: 16.79 ml 0.05 N H_2SO_4. 0.2348 g substance: 11.4 ml 0.05 N H_2SO_4. Found %: N 3.34, 3.4. $C_{23}H_{23}O_5N$. Calculated %: N 3.56.

p-Phenetide of 4,4'-dimethoxybenzilic acid. Initial substances: 5.9 g of the ethyl ester of p-ethoxyoxanilic acid, 34.8 g of iodanisole, and 3.6 g of magnesium. The phenetide is insoluble in water or gasoline, freely soluble in ether, alcohol, acetic acid, and other solvents. It colors concentrated sulfuric acid a transitory violet and concentrated phosphoric and hydrochloric acids crimson. Crystallization from alcohol yielded colorless lentil-shaped crystals in clusters. M.p. 131°. The p-phenetide of 4,4'-dimethoxybenzilic acid has not been described in the literature. The yield was 5.4 g, or 53.5% of the theoretical.

0.1735 g substance: 8.3 ml 0.05 N H_2SO_4. 0.3466 g substance: 16.15 ml 0.05 N H_2SO_4. Found %: N 3.35, 3.27. $C_{24}H_{25}O_5N$. Calculated %: N 3.44.

α-naphthalide of 4,4'-dimethoxybenzilic acid. Initial substances: 6.07 g of α-naphthyloxamic ester, 34.8 g of p-iodanisole, and 3.6 g of magnesium. The naphthalide is insoluble in water or gasoline, and soluble in alcohol, benzene, and carbon tetrachloride. It colors concentrated sulfuric acid a transitory blue-violet. It crystallizes from toluene as colorless needles with a m.p. of 177-178°. The yield was 7.1 g, or 70.3% of the theoretical. The α-naphthalide of 4,4'-dimethoxybenzilic acid has not been described in the literature.

0.4154 g substance: 20.06 ml 0.05 N H_2SO_4. 0.2541 g substance: 12.4 ml 0.05N H_2SO_4. Found %: N 3.38, 3.45. $C_{28}H_{23}O_4N$. Calculated %: N 3.39.

β-naphthalide of 4,4'-dimethoxybenzilic acid. Initial substances: 6.3 g (1 mole) of the ethyl ester of β-naphthyloxamic acid, 30.6 g (5 moles) of p-iodanisole, and 3.15 g of magnesium. The yield was 7.67 g, or 72.8% of the theoretical. The naphthalide is insoluble in water and gasoline, but soluble in other organic solvents. It dissolves in concentrated sulfuric acid, coloring it a transitory blue. It crystallizes from alcohol as colorless prisms with a m.p. of 144.5-145.5°. We are the first to have synthesized the β-naphthalide of 4,4'-dimethoxybenzilic acid.

0.5256 g substance: 12.6 ml 0.1 N H_2SO_4. 0.3321 g substance: 8.3 ml 0.1 N H_2SO_4. Found %: N 3.35, 3.26. $C_{26}H_{23}O_4N$. Calculated %: N 3.39.

3,3-Bis-(4-methoxyphenyl)-oxindole. (p-Dianisolisatin). 1 ml of a 75% solution of sulfuric acid was added to a solution of 0.15 g of the anilide of 4,4'-dimethoxybenzilic acid in 5 ml of acetic acid. The reaction mass was heated for 5-10 minutes on a water bath (60-70°) until the crimson coloring vanished completely, after which the reaction product was isolated as in the preceding experiments. The uncrystallized product fused at 148°. Minute lamellae when crystallized from ether. The crystals grow damp at 65°, fusing with frothing at 69°, then resolidifying and finally melting at 156-157°. p-Dianisolisatin was first synthesized by Baeyer and Lasarus [1], with a m.p. of 65°, by condensing isatin and anisole in the presence of concentrated sulfuric acid. Hoffmann [2] gives the m.p. of this compound as 117-118°. Inagaki [3] notes that four substances are formed when isatin is condensed with anisole. The principal product, p-dianisolisatin, crystallizes from alcohol and has a m.p. of 157° when free from alcohol. According to our findings, p-dianisolisatin forms a molecular compound with ether (m.p. 69°). Its m.p. is 156-157° when free of the crystallization ether, which agrees with Inagaki's findings.

Found %: N 3.92, 3.88. $C_{22}H_{19}O_3N$. Calculated %: N 4,06.

3,3-Bis-(4-methoxyphenyl)-5-ethoxyoxindole. The 5-ethoxy-p-dianisolisatin was synthesized by adding 2 ml of a 60% solution of sulfuric acid to a solution of 2 g of the p-phenetide of 4,4'-dimethoxybenzilic acid. This yielded 1.55 g of the substance, or 81.6% of the theoretical. The substance is soluble in alcohol, acetic acid, benzene, ether, and carbon tetrachloride. It crystallizes from alcohol as a fine crystalline powder (needles under the microscope) with a m.p. of 179-180°.

0.3004 g substance: 14.35 ml 0.05 N H_2SO_4. 0.1652 g substance: 8.1 ml 0.05 N H_2SO_4. Found %: N 3.34, 3.43. $C_{24}H_{23}O_4N$. Calculated %: N 3.6.

3,3-Bis-(4-methoxyphenyl)-7-methoxyoxindole. This was produced, as in the foregoing experiments, by condensing o-anisidine with 4,4'-dimethoxybenzilic acid, the yield being 84.2% of the theoretical. Crystallization from alcohol yields a finely crystalline powder with a m.p. of 212-213°.

0.3303 g substance: 16.53 ml 0.05 N H_2SO_4. 0.2201 g substance: 11.5 ml 0.05 N H_2SO_4. Found %: N 3.5, 3.65. $C_{23}H_{21}O_4N$. Calculated %: N 3.73.

3,3-Bis-(4-methoxyphenyl)-6-bromoxindole and 3,3-bis-(4-methoxyphenyl)-4-bromoxindole. Initial substances: 4 g of the m-bromanilide of 4,4'-dimethoxybenzilic acid, dissolved in 20 ml of acetic acid and 4 ml of concentrated sulfuric acid. Crystallization from alcohol yielded a small quantity of colorless acicular crystals with a m.p. of 198-205°. Recrystallization raised the m.p. to 209-211°. The m.p. of 3,3-bis-(4-methoxyphenyl)-4-bromoxindole is given as 211° in the literature [4]. This yielded 0.05 g of the substance, or 1.31% of the theoretical, based on the m-bromanilide used for the reaction. The principal reaction product was precipitated by diluting the filtrate with water. It crystallized from benzene as colorless needles with a m.p. of 193-194°, which is the figure given in the litera-

ture for 3,3-bis-(4-methoxyphenyl)-6-bromoxindole [4]. The yield was 2.9 g of the pure substance, or 75.6% of the theoretical.

Found %: Br 18.65. $C_{22}H_{18}O_3NBr$. Calculated %: Br 18.85.

6-Bromodianisoleisatoic anhydride. 2 ml of a 50% aqueous solution of chromic anhydride were added to a solution of 2 g of 6-bromodianisoleisatin in 16 ml of glacial acetic acid, and the reaction mass was heated for 40 minutes on a water bath. A crystalline precipitate settled out as it cooled. It crystallized from glacial acetic acid as pale-yellow prisms with a m.p. of 201-202°. The yield was 1.4 g, or 67.5% of the theoretical. The synthesized substance colored concentrated sulfuric acid bright red. These data agree with those described in the literature for 6-bromodianisoleisatoic anhydride [4].

3,3-Bis-(4-methoxyphenyl)-6,7-benzooxindole. [3,3-Bis-(4-methoxyphenyl-α-naphthoxindole]. Initial substances: a solution of 1.1 g of the α-naphthalide of 4,4'-dimethoxybenzilic acid in 15 ml of acetic acid and 1 ml of a 60% solution of sulfuric acid. The reaction mass was heated on a water bath (70-80°) until the crimson color disappeared (3 to 5 minutes). This yielded 0.98 g, or 93.5% of the theoretical, of colorless lenticular crystals (from alcohol) with a m.p. of 199-201°. The α-naphthalide of 4,4'-dimethoxybenzilic acid was condensed with equal success when phosphoric and hydrochloric acids were present.

0.2883 g substance: 15.16 ml 0.05 N H_2SO_4. 0.2161 g substance: 11.1 ml 0.05 N H_2SO_4. Found %: N 3.68, 3.59. $C_{26}H_{21}O_3N$. Calculated %: N 3.54.

3,3-Bis-(4-methoxyphenyl)-4,5-benzooxindole. [3,3-Bis-(4-methoxyphenyl)-β-naphthoxindole]. The β-naphthalide of 4,4'-dimethoxybenzilic acid was condensed by using 60% sulfuric acid and concentrated phosphoric and hydrochloric acids. We shall describe the condensation with phosphoric acid. 5 ml of phosphoric acid were added to a solution of 0.4 g of the β-naphthalide of 4,4'-dimethoxybenzilic acid in 10 ml of acetic acid. The crimson coloring vanished completely when the reaction mass was heated for 10 minutes on a water bath (70-80°). This yielded 0.3 g, or 75% of the theoretical. It crystallized from dilute acetic acid as colorless little stars with a m.p. of 270°.

0.3960 g substance: 10.3 ml 0.1 N H_2SO_4. 0.2635 g substance: 6.5 ml 0.1 N H_2SO_4. Found %: N 3.64, 3.42. $C_{26}H_{21}O_3N$. Calculated %: N 3.54.

SUMMARY

1. A new method has been elaborated for producing p-dianisoleisatin and its derivatives, and several compounds hitherto not described in the literature have been synthesized and their properties investigated.

2. The intramolecular condensation of the m-bromanilide of 4,4'-dimethoxybenzilic acid has been used to demonstrate that condensation occurs preferably at the para position to the substituent when there is a substituent in the meta position to the radical attached to the nitrogen atom.

3. The condensation of aryl amides of 4,4'-dimethoxybenzilic acid in the presence of various mineral acids (H_2SO_4, H_3PO_4, and HCl) has been used to demonstrate that the condensation is not affected by the nature of the acid anion, being governed by the internal structure of the organic cation.

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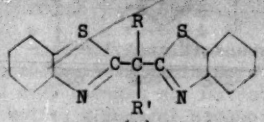
THE DERIVATIVES OF BISBENZOTHIAZOLYLMETHANE

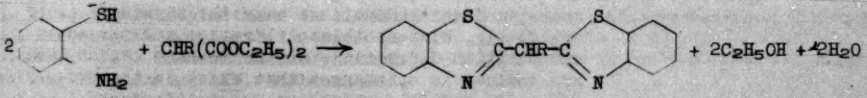
A. I. Kiprianov, L. P. Yakovleva, and Yu. S. Rozum

Bis-[benzothiazolyl-(2)]-methane was produced in 1922 by Mills [1] by condensing two molecules of o-aminothiophenol and malonic ester. Since bisbenzothiazolemethane is the basis of the monomethenylthiacyanins, which interested us in connection with the problem of the influence exerted by steric hindrances upon the color of organic dyes [2], we undertook the synthesis and spectroscopic analysis of the derivatives of bisbenzothiazolylmethane that contain one or two substituents attached to the methane carbon atom (see Formula A). No compounds of this sort are known up to the present. time. We also synthesized and investigated several new monomethenylthiacyanins containing an alkyl group at the central carbon atom.

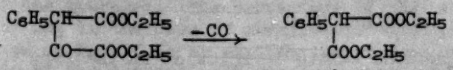


(A)

We synthesized homologs of bisbenzothiazolylmethane by condensing alkyl malonic esters with o-aminothiophenol:



We prepared alkyl malonic esters in the customary manner: by reacting alkyl halides with sodium malonic ester. Ethylmalonic, n-propylmalonic, isopropylmalonic, and dimethylmalonic esters were prepared. The pure methylmalonic ester could not be prepared by the method specified, since it was found to be impossible to separate it from the unchanged malonic ester and the dimethylmalonic ester, the boiling points of which are very close together. We therefore prepared methylmalonic ester by boiling α-cyanopropionic ester with an alcoholic solution of sulfuric acid. We prepared phenylmalonic ester by condensing ethyl oxalate with phenyl acetate and splitting off carbon monoxide from the resultant phenylketosuccinic acid [3]:



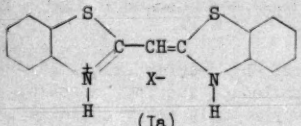
Condensation of the six malonic esters with o-aminothiophenol yielded the following bisbenzothiazolylmethanes with substituents at the methylene group: methyl-, ethyl-, n-propyl-, isopropyl-, phenyl-, and dimethylbisbenzothiazolylmethane. Condensation was effected by heating a mixture of the components to 200-220° until the calculated quantity of alcohol and water had passed through a dephlegmator. There remained within the flask an oil, which sometimes crystallized immediately, while requiring considerable effort, with prolonged refining, at others. The isopropyl derivative was not isolated in the crystalline state and therefore was not investigated further.

All these new bases proved to be nearly colorless substances with a faint yellowish tinge. They are insoluble in water, but dissolve freely in hydrochloric acid. The methyl- and ethylbisbenzothiazolylmethanes are very slightly soluble in alcohol. Table 1 gives the absorption maxima and the corresponding molecular extinctions for these bases, as well as the known unsubstituted bisbenzothiazolylmethane, as determined in alcoholic solution (with the exception of Preparations II and III, which were photographed in dioxane) with a Hilger quartz spectrograph.

TABLE 1

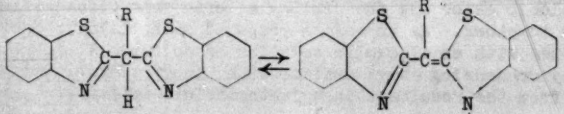
Preparation No.	R	R'	λ_{max}	ε_{max}	λ'_{max}	ε'_{max}
I	H	H	3930 Å	102	2625 Å	25000
II	CH_3	H	3740 Å	80	2690 Å	20000
III	C_2H_5	H	4030 Å	50	2690 Å	27500
IV	n-C_3H_7	H	4075 Å	40	2625 Å	25000
V	iso-C_3H_7	H	–	–	–	–
VI	C_6H_5	H	4050 Å	32	2645 Å	20000
VII	CH_3	CH_3	–	–	2625 Å	20000

The hydrogen atoms of the methylene group in the bisbenzothiazolylmethane molecule are active. One of them may be readily replaced by sodium, as is evidenced by the intensive yellow color that appears when the preparation is reacted with the alcoholic alkali. The action of mineral acids likewise produces intensely yellow salts, whose appearance and absorption curves in alcoholic solution are quite like those of the monomethenylthiacyanins, and which doubtless have the structure (Ia).



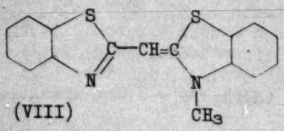
(Ia)

Apparently, bisbenzothiazolylmethane and its monosubstitution derivatives at the methane carbon atom are tautomeric substances that exist in the two forms (B) and (C), which are in equilibrium:



(B) (C)

The extent to which bisbenzothiazolylmethane exists in solution in the form (C) and how the equilibrium depends upon the nature of the substituent R may be determined from a comparison of the ultraviolet absorption curves of Preparations I-VII we have plotted with the absorption curve secured by Mills [1] for Preparation (VIII): The respective curves are reproduced in Fig. 1.



(VIII)

Preparation (VIII) has structure C, as determined by the substitution of a methyl group for the hydrogen atom attached to the nitrogen. Preparation (VII), on the other hand has the fixed form B. There is a substantial difference between their absorption curves. Preparation (VII) absorbs only beyond 3000 Å, whereas the absorption curve for Preparation (VIII) exhibits a very strong band at the edge of the visible region of the spectrum. The other bisbenzothiazolylmethanes (I-VII) all exhibit, in addition to their strong absorption in the shortwave region of the spectrum, a weak absorption band with its maximum at the edge of the visible region, evidence, no doubt, of the presence of some of Form C in equilibrium with Form B. Comparison of the intensity of absorption of Preparation (VIII) at the longer wavelengths with the intensity of corresponding band in bisbenzothiazolyl-

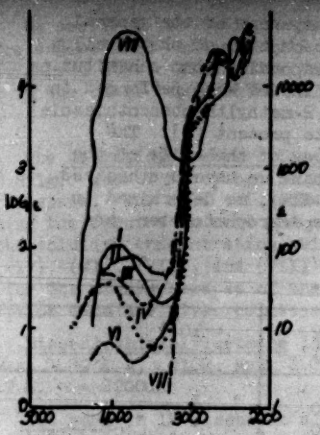


Fig. 1

I. Bisbenzothiazolylmethane in alcohol; II. Bisbenzothiazolylmethylmethane in dioxane; III. Bisbenzothiazolylethylmethane in dioxane; IV. Bisbenzothiazolyl-n-propylmethane in alcohol; VI. Bisbenzothiazolylphenylmethane in alcohol; VII. Bisbenzothiazolyldimethylmethane in alcohol; VIII. 2-[N-methylbenzothiazolidene]-methylbenzothiazole in alcohol.

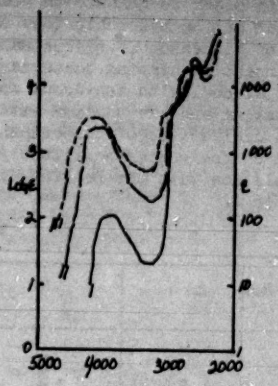
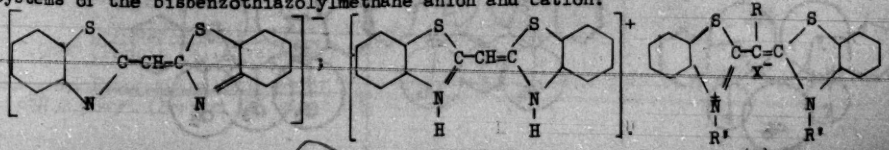


Fig. 2

I. Bisbenzothiazolylmethane in alcohol; II. Ditto in 1M alcoholic alkali; III. Ditto in 0.05M alcoholic sulfuric acid.

methane indicates that bisbenzothiazolylmethane contains only very little of Form C. The percentage of Form C in the mono substitution derivatives of bisbenzothiazolylmethane is even smaller, diminishing with the size of the radical introduced in place of the hydrogen. The percentage of the tautomeric form C in the solution is extremely low in the case of phenylbenzothiazolylmethane. When we consider that the percentage of Form C in an equilibrium mixture of the two tautomers is determined by the ratio of the intensity of the long-wave absorption band of the given derivative of bisbenzothiazolylmethane to the intensity of the absorption band of Preparation (VIII) (which is only approximately correct), we find that there is 0.3% of Form C in the unsubstituted bisbenzothiazolylmethane, while its phenyl derivative contains about 0.01%. The reason for substituents shifting the tautomeric equilibrium to the left is apparently the former's electronic influence. The same effect has been observed in substituents at the methylene group in derivatives of acetylacetone [4].

Figure 2 gives the absorption curves of bisbenzothiazolylmethane in neutral, alkaline, and acidic alcoholic solutions. The absorption is very much alike in the alkaline and acidic solutions, both in the shape of the curves and in the magnitude of the molecular extinction. This is due to the similarity of the chromophoric systems of the bisbenzothiazolylmethane anion and cation:



(D)

We have synthesized various monomethenylthiacyanins of the general formula (D) in order to be able to compare the absorption of these yellow dyes with that of the hydrochlorides of the corresponding mono substitution derivatives of bisbenzothiazolylmethane. The syntheses were performed in the usual manner: by heating quaternary salts of 2-methylthiobenzothiazole dissolved in alcohol with anhydrous sodium acetate present [5]. The absorption maxima and the maximum extinction values of the salts of the substitution derivatives of bisbenzothiazolylmethane we have synthesized (IX-XII) and of the monomethenylthiacyanins (XII-XIX), as determined in alcoholic solution with the Bellingham—Stanley spectrophotometer, are given in Table 2.

Table 2

Preparation No.	R	R'	λ_{max} (Å)	$\varepsilon \cdot 10^{-4}$
IX	H	H	4250	1
X	CH_3	H	4250	1
XI	C_2H_5	H	4220	1
XII	n-C_3H_7	H	4270	1
XIII	H	CH_3	4250	8.1
XIV	H	C_2H_5	4250	7.5
XV	H	n-C_3H_7	4280	7.3
XVI[2]	CH_3	CH_3	4650	4.7
XVII	C_2H_5	CH_3	4650	4.7
XVIII	n-C_3H_7	CH_3	4660	4.5
XIX	CH_3	C_2H_5	4800	4.3

Inspection of Table 2 indicates that substitution for the hydrogen atoms in the methenyl group when there are no radicals attached to the nitrogen atoms (IX-XII), has practically no effect on the absorption maximum or on its intensity, exactly as is the case when alkyl groups are introduced at the nitrogen atoms when there are no substituents in the methenyl group (XII-XV). But as soon as we introduce alkyl groups at the nitrogen atoms and into the methenyl group at the same time (XVI-XIX), the color grows much deeper (turning from yellow to orange); and the intensity is halved. There is no doubt that the causes of these singular optical properties of the last four preparations in Table 2 are the steric hindrances produced by the coplanar arrangement of the heterocyclic rings with the radicals introduced into the molecule. Similar phenomena have already been observed in monomethenylthiacyanins and in trimethenylthiacyanins by Kiprianov and Ushenko [2] and in quinocyanins by Brooker and his associates [6].

The drawing reproduced herewith indicates the molecular structure of the salts of monosubstitution derivatives of the monomethenylthiacyanins (Fig. 3), the monomethenylthiacyanins without any substituent in the methenyl group (Fig. 4), and the monomethenylthiacyanins with substituents in the methenyl group (Fig. 5).

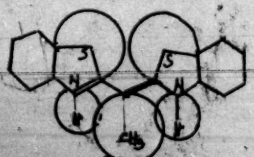


Fig. 3.

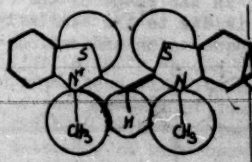


Fig. 4.

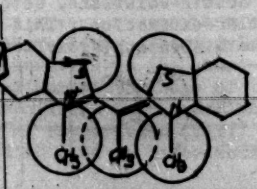


Fig. 5.

[1] The molecular extinction could not be determined owing to alcoholysis of the salt.

We see from these diagrams, in which the dimensions of the bonds, valence angles, and radical radii are shown approximately to scale, that the strongest steric hindrances to a planar arrangement of the molecule arise in the cases represented in Fig. 5 (Preparations XVI-XIX in Table 2).

EXPERIMENTAL

The ultraviolet absorption spectra were photographed with a standard E-298 Hilger quartz spectrograph fitted with a Goode sector photometer and a wolfram spark. The cell thickness was varied from 0.01 to 5 cm when photographing the spectra in acid and alkaline solutions, both the cell thickness and the solution concentration being varied in neutral solvents. The compounds (I), (IV), (VI), (VII), and (VIII) were recorded in 96% alcohol, dioxane being used for the others because of their poor solubility in alcohol. The numerical absorption data are given below.

Bisbenzothiazolylmethane in alcohol, 10^{-2} to 10^{-3} mole per liter (Fig. 1, I): Max. 1.3930 A, ε=102; Max. 2.2625 A, ε=25000; Min. 1.3340 A, ε=20; Min. 2.2517 A, ε = 20000.

The same in 1M alcoholic alkali, 10^{-2} mole per liter (Fig. 2, II): Max. 1.4180 A, ε=3000; Max. 2.2665 A, ε=20000; Min. 1.3400 A, ε=550; Min. 2.2475 A, ε=13000.

The same in 0.05M alcoholic acid (sulfuric), 5.10^{-3} mole per liter (Fig. 2, III): Max. 1.4105 A, ε=2000; Max. 2.2630 A, ε=19000; Min. 1.3300 A, ε=170; Min. 2.2500 A, ε=16000.

Bisbenzothiazolylmethylmethane in dioxane, 10^{-3} to 2.10^{-4} mole per liter (Fig. 1, II). Max. 1.3740 A, ε=80; Max. 2.2690 A, ε=20000; Min. 1.3380 A, ε=50; Min. 2.2490 A, ε=1150.

Bisbenzothiazolylethylmethane in dioxane, 2.10^{-3} mole per liter (Fig. 1, III). Max. 1.4030 A, ε=50; Max. 2.2690 A, ε=27500; Min. 1.3580 A, ε=25; Min. 2.2510 A, ε=20000.

Bisbenzothiazolyl-n-propylmethane in alcohol, 10^{-2} mole per liter (Fig. 1, IV). Max. 1.4075 A, ε=35; Max. 2.2625 A, ε=25000; Min. 1.3485 A, ε=5.5; Min. 2.2445 A, ε=13000.

Bisbenzothiazolylphenylmethane in alcohol, 5.10^{-3} mole per liter (Fig. 1, VI). Max. 1.4050 A, ε=6.4; Max. 2.2645 A, ε=20000; Min. 1.3725 A, ε=4.0; Min. 2.2480 A, ε=13000.

Bisbenzothiazolyldimethylmethane in alcohol, 5.10^{-2} to 10^{-3} mole per liter (Fig. 1, VII). Max. 2625 A, ε=20000; Min. 2473 A, ε=13000.

2-[N-Methylbenzothiazolidene]-methylbenzothiazole in alcohol, 10^{-3} mole per liter (Fig. 1, VIII). Max. 1.3795 A, ε=45000; Max. 2.2463 A, ε=40000; Min. 1.3085 A, ε=1300; Min. 2.2320 A, ε=20000.

Methylmalonic ester was prepared from α-bromopropionic ester via cyanopropionic ester [7]. B.p. 74° at 3 mm, d_{25}^{25} 1.0131 (Perkin [8] gives d_{25}^{25} 1.01295).

Ethylmalonic ester [9] was prepared with a b.p. of 88-89° at 8 mm, d_{20}^{20} 1.0027 (Michael [10] gives d_{20}^{20} 1.004).

n-Propylmalonic ester [11] was prepared with a b.p. of 222°, d_{25}^{25} 0.9860 (Perkin [8] gives d_{25}^{25} 0.9854).

Isopropylmalonic ester [12] was prepared with a b.p. of 213-214°, d_{25}^{25} 0.98495 (Perkin [8] gives d_{25}^{25} 0.98521).

Phenylmalonic ester [3] was prepared with a b.p. of 145-148° at 6 mm, d_{20}^{20} 1.0946 (Berkenheim gives d_{20}^{20} 1.095).

Dimethylmalonic ester [13] was prepared with a b.p. of 193-195°, d_{25}^{25} 0.9928 (Perkin [8] gives d 0.9935).

Bis-[benzothiazolyl-(2)]-methane and the bis-[benzothiazolyl-(2)]-alkylmethanes were prepared as follows. 2 moles of o-aminothiophenol and 1 mole of malonic, alkyl malonic, or phenylmalonic ester were heated in a current of CO_2 for 1-3 hours to about 200° in a flask fitted with a dephlegmator and a straight condenser, the water and alcohol being gradually distilled off through the dephlegmator. Heating was stopped as soon as approximately the calculated quantity of distillate had accumulated in the receiver. The oil left in the flask was washed with a 10% solution of sodium hydroxide to eliminate the unreacted o-aminothiophenol. The oil was then purified by converting it into a yellow crystalline hydrochloride by the action of concentrated hydrochloric acid (this refining was unnecessary for bisbenzothiazolylmethane and bisbenzothiazolyldimethylmethane), the hydrochloride being recrystallized from absolute alcohol. Then the pure salt was decomposed with soda or pyridine, after which the base usually crystallized. In some cases crystallization was speeded up by adding a few drops of water, acetone, or pyridine. The refining methods, melting points, yields, and percentages of nitrogen in the bases we synthesized are listed in Table 3.

Table 3

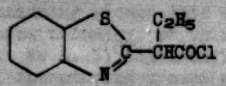
Preparation No.	Refining Method	M.p. (°C)	Yield, % of the theoretical	Empirical Formula	% Nitrogen Experimental	% Nitrogen Calculated
I	Crystallization from alcohol	93°	75	$C_{15}H_{12}N_2S_2$	9.48 9.50	9.46
II	Crystallization from aqueous pyridine	165	86	$C_{15}H_{12}N_2S_2$	9.48 9.50	9.46
III	Crystallization of the HCl salt from absolute alcohol	158	—	$C_{17}H_{14}N_2S_2$	8.86 8.87	9.03
IV	Crystallization from aqueous alcohol	92	61.5	$C_{18}H_{16}N_2S_2$	8.63 8.82	8.64
V	Distillation in vacuo	b.p.220	46	$C_{18}H_{16}N_2S_2$	8.46 8.48	8.64
VI	Crystallization from petroleum ether	140	94	$C_{21}H_{14}N_2S_2$	7.85 7.93	7.82
VII	Crystallization from alcohol	157	75	$C_{17}H_{14}N_2S_2$	9.02 9.14	9.03

2-[N-Methylbenzothiazolidene]-methylbenzothiazole (VIII) was prepared by the Mills method [1]; but we methylated the bisbenzothiazolylmethane with dimethyl sulfate instead of with methyl iodide. Two grams of bisbenzothiazolylmethane yielded 0.4 g of the base (VIII) with a m.p. of 174° (Mills gives 172°).

The monomethenylthiacyanins were prepared by the Kendall method [5]. Absolute alcohol was added to a mixture consisting of 1 mole of a quaternary

salt of a 2-alkylbenzothiazole, 1 mole of a quaternary salt of 2-methylthiobenzothiazole[1], and 3 moles of anhydrous sodium acetate, and the mixture was then boiled for 1-2 hours. A thiol separated out, the mixture turning a bright orange. Most of the alcohol was driven off, and potassium iodide was added to the mixture; crystals of a dye--an iodide that was refined by crystallization from alcohol--settled out after some time had passed. The preparation (XVIII) was refined chromatographically in chloroform on alumina. Our observations indicate that some of an iodide dye may be converted into a chloride during this procedure. We therefore used a perchlorate of the dye (XVIII) in chromatography.

We tried to synthesize N,N'-dimethyl-α-ethylmonomethenylthiacyanin iodide by condensing two moles of N-methyl-o-aminothiophenol [4] with ethylmalonyl chloride. Steric hindrances apparently prevented condensation of more than one molecule of the N-methyl-o-aminothiophenol, however. Hydrolysis and the loss of CO_2 converted the resulting acid chloride (XX) into 2-n-propylbenzothiazole chloromethylate.



(XX)

The refining methods, melting points, yields and analysis results are given in Table 4 for the monomethenylthiacyanins we have synthesized.

SUMMARY

Six new bases--derivatives of bisbenzothiazolylmethane substituted at the methane residue--have been synthesized by condensing orthoaminothiophenol with esters of methylmalonic, ethylmalonic, n-propylmalonic, isopropylmalonic, phenylmalonic, and dimethylmalonic acids. The ultraviolet absorption curves of bisbenzothiazolylmethane and of six of its derivatives have been recorded and compared with the absorption curve for 2-[N-methylbenzothiazolidene-(2)]-methylbenzothiazole. It has been shown that bisbenzothiazolylmethane and its monosubstitution derivatives exhibit tautomerism in solution.

Three new monomethenylthiacyanins, containing alkyl groups as substituents attached to the central carbon atom, have been synthesized. Their absorption curves in alcoholic solutions have been recorded, and it has been shown that steric hindrances exist in the molecules of these dyes which prevent the coplanarity of the thiazole rings.

Table 4[2]

Preparation No.	Refining Method	M.P. (°C)	Yield % of the theoretical	Empirical Formula	Analysis results: Experimental	Analysis results: Calculated
XIV	Crystallization from alcohol	298°	43	$C_{19}H_{19}N_2S_2I$	I 27.44 27.49	I 27.25
XV	Crystallization from alcohol	274	57	$C_{21}H_{23}N_2S_2I$	—	—
XVII	Crystallization from alcohol	206	17	$C_{19}H_{19}N_2S_2I$	I 27.20 27.01	I 27.25
XVIII	Chromatography on Al_2O_3	187	—	$C_{20}H_{21}O_4N_2S_2Cl$	Cl 9.02 8.12	Cl 7.85
XIX	Crystallization from alcohol	213	—	$C_{20}H_{21}N_2S_2I$	I 26.24 26.26	I 26.45

[1]) Alkyl sulfates are the best quaternary salts for synthesizing the preparations (XVI-XIX). Chlorides, bromides, and iodides do not form dyes.

[2]) I.K.Ushenko assisted in the synthesis of Preparations XIV and XV.

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RESEARCHES ON CYANIN DYES

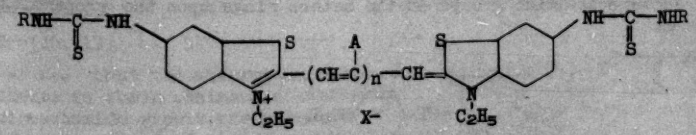
V. THIACYANIN DYES CONTAINING THIOCARBAMIDE GROUPS

N. F. Turitsyna and I. I. Levkoev

Many cyanin dyes--derivatives of benzothiazole that are effective sensitizers--also exert a favorable effect upon the overall photo sensitivity of silver halide emulsions [1-5], which is far from typical of other classes of optical sensitizers. In view of the property of some sulfur compounds of increasing the photosensitivity of silver-halide emulsions [6], the hypothesis has been advanced that the high activity of the thiacyanins is related to the presence of sulfur atoms in their molecules [8]. This would make it of interest to attempt the accumulation of sulfur atoms in thiacyanin molecules or to introduce sulfur-containing groups into other types of sensitizing dyes. Similar dyes containing thioalkyl or thioaryl groups have been proposed in several patents [7]. As A. I. Kiprianov, Z. P. Sytnik, and E. D. Sych [8] have shown, however, introducing groups of this sort has no substantial effect upon the properties of dyes.

The nature of the sulfur atoms in thiacyanins and in the above-mentioned dyes containing thio ester groups differs greatly, however, from that in Sheppard's chemical sensitizers [6] (thiocarbamides, thiosulfates, etc.). In the latter, the sulfur, which is usually attached by a double bond, may be split off readily, so that silver sulfide may be formed in silver halide emulsions when these substances are present. Though the formation of silver sulfide in photographic emulsions may not be the basic reason for their high photosensitivity [9], there is no doubt that it may influence the sensitivity appreciably.

We were therefore interested in synthesizing cyanin dyes containing groups with "labile" sulfur in order to test the feasibility of combining the properties of an optical and a chemical sensitizer within a single dye molecule. With this in mind we synthesized and investigated the properties of thiacyanin dyes that had heterocyclic residues of allyl- and benzylthiocarbamide groups at the 6,6' positions (I).

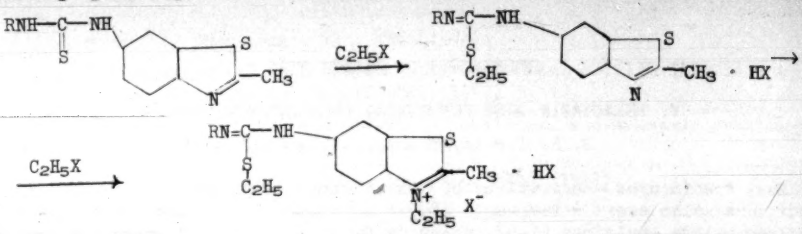


(I)

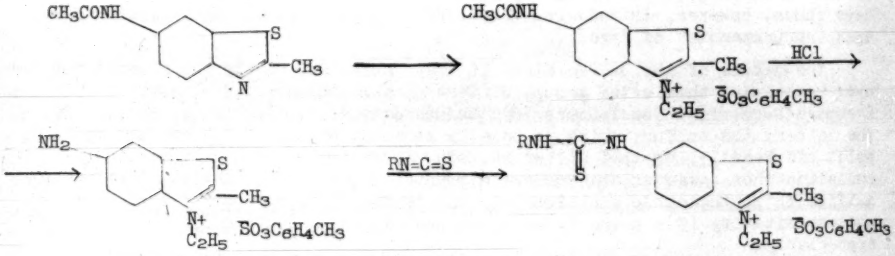
where R = C_3H_5 or $C_6H_5CH_2$; A = H, CH_3, or C_2H_5; and X = an anion.

The quaternary salts of 6-allyl- and 6-benzylthiocarbamido-2-methylbenzothiazole and the respective bases required for the synthesis of these dyes are not described in the literature. We produced these bases readily by reacting 6-amino-2-methylbenzothiazole with allyl and benzyl thiocyanates in alcohol [10]. We were unable, however, to synthesize the corresponding quaternary salts from them by the action of esters of p-toluenesulfonic acid or other alkylating agents. We found that in such a reaction S-alkylisothiocarbamide derivatives are produced most easily [11], being converted to the corresponding quaternary salts when the

alkylating agent is present in excess:

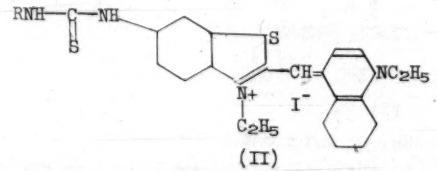


We succeeded in preparing the 6-allyl- and 6-benzyl-S-ethylisothiocarbamido-2-methylbenzothiazoles and the corresponding quaternary salts in the pure state. The quaternary salts of 6-allyl- and 6-benzylthiocarbamido-2-methylbenzothiazole were successfully prepared by reacting allyl and benzyl thiocyanates with quaternary salts of 6-amino-2-methylbenzothiazole. The latter were prepared by saponifying quaternary salts of 6-acetamino-2-methylbenzothiazole with hydrochloric acid.

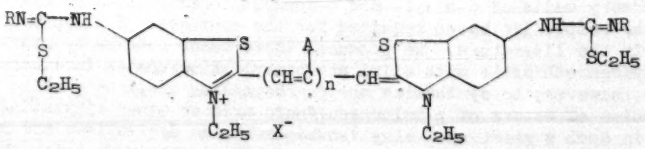


The foregoing quaternary salts were used to synthesize carbo- (I, n = 1; A = H, CH_3, or C_2H_5), and di- and tricarbocyanins (I, n=2 or 3; A = H), as well as isocyanins (II) by the usual methods.

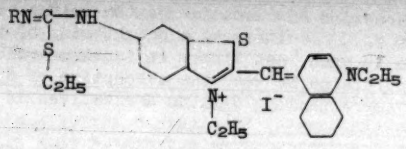
We also synthesized analogous dyes containing allyl- and benzyl-S-ethylisothiocarbamide groups (III and IV) to determine the effect of the presence of isothiocarbamide groups in the hetero rings upon the properties of the cyanins.



(II)



(III)



(IV)

The absorption maxima of the carbo-, dicarbo-, and isocyanins are listed in Table 1 together with the maxima for the corresponding dyes with no substituents in the hetero rings and for some 6,6'-diamino- and 6,6'-diacetamino derivatives.

Table 1

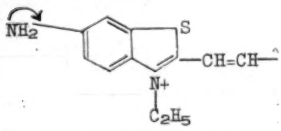
Positions of the Absorption Maxima of Thiacyanin Dyes With N-Alkylthio and N,S-Dialkylisothiocarbamide Groups at the 6,6' Positions, as well as of the Corresponding Dyes Without any Substituents in the Heterocyclic Rings of the Dyes and of Some 6,6'-Diamino- and 6,6'-Diacetamino Derivatives

Substituents at the 6,6' positions of the benzothiazole ring	Positions of the absorption maxima, mμ				
	Carbocyanins with substituents at the 9 position			Dicarbocyanins	Isocyanins
	H	CH_3	C_2H_5		
H	557.5[12]	543.5[12]	547.5[12]	650 [13]	503 [13]
$C_3H_5-NH-C(=S)-NH-$	578	566	570	667	507
$C_3H_5-N=C(SC_2H_5)-NH-$	586	573	578	677	519
$C_6H_5CH_2-NHC(=S)-NH-$	578	566	570	669	508
$C_6H_5CH_2-N=C(SC_2H_5)-NH-$	586	573	578	680	519
NH_2—[14, 15]	594	—	—	688	—
CH_3CONH—[16, 17]	577	—	—	670	512

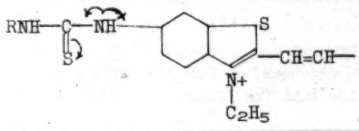
We see that the absorption maxima for the thiacarbocyanins without substituents in their chains are shifted 20.5 mμ toward longer wavelengths when alkylthiocarbamide groups are added at the 6,6' positions. S-Ethylisothiocarbamide groups produce a much greater bathochromic shift, totaling 28.5 mμ. In the isocyanins, the S-ethylisothiocarbamide group produces a shift of about 16 mμ, while the thiocarbamide group causes a shift of only 4-5 mμ. In contrast to the 6,6'-diaminothiacarbocyanins, the absorption maxima of the dyes that contain thio- and isothiocarbamide groups are shifted appreciably toward the shorter wavelengths, like the other acylamino derivatives [14,17,18].

As was first noted by A. I. Kiprianov [14], the deep color of 6,6'-diaminothiacarbocyanins is apparently due to a shift of electrons from the nitrogen atom of the amino group to the polymethine chromophore, as represented by Formula (V). In dyes that contain thiocarbamide groups this shift is

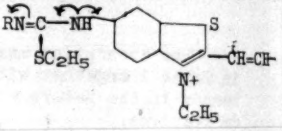
diminished because of the attraction of electrons to the sulfur atoms of the thiocarbamide groups (Formula VI), resulting in a heightening of the color. Such a diversion of electrons is much less likely in isothiocarbamide groups (Formula VII), so that the difference between the absorption of dyes containing these groups and that of the corresponding diamino derivatives is diminished substantially.



(V)



(VI)



(VII)

Photographic tests of the synthesized dyes have shown that in some instances the introduction of N-alkylthio and N,S-dialkylisothiocarbamide groups into the molecule of thiacyanin dyes increases their ability to act as optical sensitizers. S-Ethyl-N-alkylisothiocarbamide derivatives are much more effective, as a rule. The sensitizing ability of dyes containing N-alkylthio- and N-allyl-S-ethylisothiocarbamide groups is usually higher than that of the corresponding N-benzyl derivatives, which is apparently due, to a certain extent, to the lower solubility of the latter. Like other acylaminothiacyanins [19], none of the synthesized dyes possesses any appreciable second-order sensitizing ability. We found, however, that dyes containing N-alkylthiocarbamide groups do not increase the overall sensitivity of silver halide emulsions substantially, and hence, are not chemical sensitizers. Nor does the introduction of these dyes into an emulsion cause much of an increase in fog density.

EXPERIMENTAL

2-Methyl-6-aminobenzothiazole ethyl-p-tolusulfonate hydrochloride. A mixture of 8.70 g of 2-methyl-6-acetaminobenzothiazole and 8.88 g of the ethyl ester of p-toluenesulfonic acid was heated to 120-135° for 6 hours. The salt was dissolved in 175 ml of hydrochloric acid (sp. gr. 1.19), and the liquid was refluxed for 4 hours. Evaporation and vacuum drying yielded 16.5 g (97% of the theoretical). Colorless crystals with a m.p. of 202° (from absolute alcohol), readily soluble in water, more sparingly in absolute alcohol.

Found %: N 7.06; Cl 9.01. $C_{17}H_{21}N_2O_3S_2Cl$. Calculated %: N 6.99; Cl 8.85.

2-Methyl-6-aminobenzothiazole ethylperchlorate. This was prepared by adding sodium perchlorate to a solution of 1.88 g of 2-methyl-6-aminobenzothiazole ethyl-p-tolusulfonate hydrochloride in 15 ml of water with 1.5 g of pyridine present. The yield was 1.1 g, or 80.3% of the theoretical. Colorless crystals (from water). M.p. 204°.

Found %: N 9.37. $C_{10}H_{13}O_4N_2SCl$. Calculated %: N 9.57.

Ethiodide. Colorless crystals (from ethyl alcohol), m.p. 241°.

Found %: N 8.44. $C_{10}H_{13}N_2SI$. Calculated %: N 8.75.

2-Methyl-6-(N-allylthiocarbamide-N')-benzothiazole was prepared by heating a mixture of 0.50 g of 2-methyl-6-aminobenzothiazole, 0.31 g of allyl mustard oil, and 2.5 ml of ethyl alcohol for 1 hours on a boiling water bath in a flask fitted with a reflux condenser. After the mixture had cooled, the precipitate

was filtered out and washed with alcohol and ether. The yield was 0.63 g (78.5% of the theoretical). Colorless prisms (from ethyl alcohol, m.p. 156°. Slightly soluble in ether.

Found %: N 15.86, 15.73. $C_{12}H_{13}N_3S_2$. Calculated %: N 15.96.

2-Methyl-6-(N-allylthiocarbamido-N')-benzothiazole ethyl-p-tolusulfonate. A solution of 16.5 g of 2-methyl-6-aminobenzothiazole ethyl-p-tolusulfonate hydrochloride in 45 ml of absolute ethyl alcohol was boiled for 5 hours in a flask fitted with a reflux condenser (bath temperature 100-110°) with 4.4 ml of pyridine and 8.08 g of allyl mustard oil. Then the reaction product was precipitated with anhydrous ether and recrystallized from absolute ethyl alcohol. The yield was 11.4 g (60% of the theoretical). Colorless crystals (from alcohol), m.p. 175°. Readily soluble in water and alcohol.

Found %: C 54.22; H 5.30; N 9.14. $C_{21}H_{25}O_3N_3S_3$. Calculated %: C 54.38; H 5.43; N 9.07.

The ethylperchlorate was prepared by adding sodium perchlorate to an aqueous solution of the preceding compound (70% of the theoretical yield). Colorless prisms (from ethyl alcohol), m.p. 139°.

Found %: N 10.65. $C_{14}H_{18}O_4N_3S_2Cl$. Calculated %: N 10.78.

The ethiodide was prepared like the preceding compound. M.p. 179°.

Found %: N 9.79. $C_{14}H_{18}N_3S_2I$. Calculated %: N 10.02.

2-Methyl-6-(N-benzylthiocarbamide-N')-benzothiazole was prepared by heating 0.41 g of 2-methyl-6-aminobenzothiazole with 0.45 g of benzyl mustard oil and 1.5 ml of absolute ethyl alcohol for 3 hours on a boiling water bath. The yield was 0.72 g (92.0% of the theoretical). Colorless transparent leaflets (from ethyl alcohol), m.p. 191°. Slightly soluble in ether.

Found %: N 13.71, 13.76. $C_{18}H_{15}N_3S_2$. Calculated %: N 13.41.

2-Methyl-6-(N-benzylthiocarbamido-N')-benzothiazole ethyl-p-tolusulfonate. This was prepared by boiling a solution of 3.34 g of 2-methyl-6-aminobenzothiazole ethyl-p-tolusulfonate hydrochloride in 7 ml of absolute ethyl alcohol for 4 hours with 0.68 ml of pyridine and 1.78 g of benzyl mustard oil. The product was precipitated with ether and washed with acetone. The yield was 2.6 g (60.7% of the theoretical). Colorless crystals (from ethyl alcohol). M.p. 200°.

Found %: C 58.43, 58.11; H 5.74, 5.63; N 8.46, 8.34. $C_{25}H_{27}N_3O_3S_3$. Calculated %: C 58.43; H 5.30; N 8.19.

The ethiodide was prepared by precipitating a solution of the preceding compound with potassium iodide (93% of the theoretical yield). Colorless transparent leaflets (from ethyl alcohol). M.p. 200°.

2-Methyl-6-(N-allyl-S-ethylisothiocarbamido-N')-benzothiazole. A mixture of 2.1 g of 2-methyl-6-(N-allylthiocarbamido-N')-benzothiazole and 1.60 g of the ethyl ester of p-toluenesulfonic acid was heated to 130-140° for 6 hours. The salt was dissolved in water (60 ml), the odor of ethyl mercaptan being noticed, and 3 ml of pyridine was gradually added to the aqueous solution after it had been decolorized with charcoal. The light-yellow oil that separated out crystallized upon standing. The yield was 1.01 g (43.4% of the theoretical). Colorless prisms with a m.p. of 79° (from gasoline). Readily soluble in alcohol, acetone, and ether, less so in gasoline, insoluble in water.

Found %: N 14.48, 14.21. $C_{14}H_{17}N_3S_2$. Calculated %: N 14.42.

No precipitate is formed when sodium perchlorate is added to the aqueous filtrate, evaporated to small volume, which indicates that no quaternary salt

is present.

In other experiments we secured the p-toluenesulfonate of this base. A solution of 1.31 g of 2-methyl-6-(N-allythiocarbamido-N')-benzothiazole and 1.00 g of the ethyl ester of p-toluenesulfonic acid in 15 ml of absolute ethyl alcohol was refluxed for 1.5 hours. Driving off the alcohol in vacuo and crystallizing from acetone yielded 0.85 g (36.7% of the theoretical) of colorless prisms with a m.p. of 149° (from acetone). Readily soluble in alcohol, less so in water and acetone.

Found %: N 9.17, 9.10. $C_{14}H_{17}N_3S_2 \cdot C_7H_8O_3S$. Calculated %: N 9.07.

Adding 0.07 ml of pyridine to a solution of 0.36 g of the salt in 2 ml of alcohol yielded 0.18 g (79.5% of the theoretical) of 2-methyl-6-(N-allyl-S-ethylisothiocarbamido-N')-benzothiazole, m.p. 79°.

2-Methyl-6-(N-allyl-S-ethylisothiocarbamido-N')-benzothiazole ethylperchlorate. A mixture of 2.10 g of 2-methyl-6-(N-allylthiocarbamido-N')-benzothiazole and 3.21 g of ethyl p-toluenesulfonate was heated to 130-140° for 6 hours. The hyaline mass was dissolved in 20 ml of water and 2 ml of pyridine were added, followed by 1.5 g of sodium perchlorate. The resulting precipitate was filtered out and washed with water and ether. The yield was 2.31 g (68% of the theoretical). Colorless leaflets (from alcohol). M.p. 149°. Rather easily soluble in alcohol and water.

Found %: N 9.81, 10.00. $C_{18}H_{22}O_4N_3S_2Cl$. Calculated %: N 10.01.

This same product was also prepared by heating 2-methyl-6-(N-allyl-S-ethylisothiocarbamido-N')-benzothiazole p-toluenesulfonate to 130-140° with 0.13 g of ethyl p-toluenesulfonate for 6 hours, followed by dissolving the resultant hyaline mass in water, adding pyridine, and precipitating with sodium perchlorate (36.8% of the theoretical yield). The acrid odor of ethyl mercaptan was observed when the hyaline reaction mass was dissolved in water in both experiments.

2-Methyl-6-(N-benzyl-S-ethylisothiocarbamido-N')-benzothiazole. This was prepared, like the allyl derivative, by heating a mixture of 2-methyl-6-(N-benzylthiocarbamido-N')-benzothiazole (1.56 g) and ethyl p-toluenesulfonate (1.0 g), followed by treatment with pyridine (0.45 ml). The yield was 43% of the theoretical. Colorless crystals with a m.p. of 98° (from gasoline). Readily soluble in alcohol and acetone, less so in ether and gasoline, insoluble in water.

Found %: N 12.17, 12.32. $C_{18}H_{18}N_3S_2$. Calculated %: N 12.31.

We were unable to detect the presence of any perceptible amount of a quaternary salt in the filtrate of the base. It should be added that the odor of ethyl mercaptan was perceptible here again.

2-Methyl-6-(N-benzyl-S-ethylisothiocarbamido-N')-benzothiazole ethyl-p-toluenesulfonate. A mixture of 4.7 g of 2-methyl-6-(N-benzylthiocarbamido-N')-benzothiazole and 6.0 g of ethyl p-toluenesulfonate was heated to 120-128° for 7 hours. The salt was dissolved in 100 ml of boiling water, and 3 ml of pyridine were added to the solution. After the solution had cooled, the precipitate was filtered out and washed with water and ether. The yield was 5.68 g (70% of the theoretical). Slightly yellowish crystals (from alcohol), m.p. 199.5°, rather sparingly soluble in water.

Found %: N 7.57, 7.64. $C_{27}H_{31}O_3N_3S_3$. Calculated %: N 7.76.

Ethiodide--colorless crystals (from alcohol), m.p. 191°.

Found %: N 8.30, 8.37. $C_{20}H_{24}N_3S_2I$. Calculated %: N 8.45.

The following quaternary salts were used in synthesizing the dyes: I) 2-methyl-6-(N-allylthiocarbamido-N')-benzothiazole ethyl-p-toluenesulfonate; II) 2-methyl-6-(N-allyl-S-ethylisothiocarbamido-N')-benzothiazole ethylperchlorate; III) 2-methyl-6-(N-benzylthiocarbamido-N')-benzothiazole ethyl-p-toluenesulfonate; and IV) 2-methyl-6-(N-benzyl-S-ethylisothiocarbamido-N')-benzothiazole ethyl-p-toluenesulfonate. These salts are denoted by the foregoing Roman numerals in Tables 2-5.

The carbocyanins were synthesized by heating the quaternary salts (0.01 mole) with the ethyl esters of orthoformic, orthoacetic, and orthopropionic acids (0.002 mole) (denoted by the numerals 1, 2, and 3 in Table 2) to 130-140° in pyridine for 30 minutes. After the reaction mixture had cooled, it was diluted with ether (30 ml), and the precipitated dye was washed with ether and water (20 ml) and refined by crystallization from ethyl alcohol (refining Method A) or by reboiling it with small quantities of ethyl alcohol (refining Method B) until its melting point remained constant. In some cases the p-toluenesulfonates of the dyes were converted into the less soluble bromides or iodides by precipitating them with potassium bromide or iodide in a water-alcohol solution. The preparative conditions, yields, properties and analysis results are given in Table 2 for the carbocyanins we have synthesized.

Dicarbocyanins. The dicarbocyanins were synthesized by heating equimolecular quantities of the quaternary salt and β-ethoxyacrolein diethyl acetal (0.001 mole of each) in pyridine to 130-135° for 30 minutes [21,22]. The dyes were precipitated with ether (20 ml) and washed with ethyl alcohol (2-3 ml), water (50 ml), acetone (1-2 ml), and anhydrous ether. The dyes were purified by crystallizing them from methanol or ethyl alcohol (refining method A) or by rewashing them with small quantities of boiling methanol (refining Method B). The data for the dicarbocyanins synthesized are found in Table 3.

Tricarbocyanins. These dyes were synthesized in two ways: 1) by boiling a solution of 0.01 mole of the quaternary salt and 0.005 mole of glutaconylidenedianiline hydrochloride in 5 ml of absolute ethyl alcohol with a solution of 0.01 mole of sodium ethylate in 1 ml of ethyl alcohol for 4 minutes [23]; and 2) by boiling a solution of 0.02 mole of the quaternary salt and 0.01 mole of glutaconylidenedianiline in absolute ethyl alcohol for 5-8 minutes. In both procedures the precipitated dye was allowed to cool, and then filtered out and washed with water, alcohol, and ether. The dye was purified by crystallizing it from methanol (refining Method A) or by rewashing it with boiling methanol (refining Method B). The data for the tricarbocyanins synthesized are found in Table 4.

Isocyanins. These were synthesized by boiling a solution of the quaternary salt (0.001 mole) and quinoline ethiodide (0.002 mole) in absolute ethyl alcohol (5 ml) with a solution of sodium ethylate (0.002 mole in 1.5 ml of ethyl alcohol) for 20 minutes. After the mixtures had cooled, the precipitated dyes were filtered out, washed with alcohol, water, and ether, and refined by crystallizing them from methanol. The yields of these dyes and their properties are given in Table 5, together with the results of their analyses.

The authors wish to express their profound gratitude to Academician V. M. Rodionov for his invaluable counsel in the carrying out of the present research and for his unflagging interest in it.

Table 2

Synthesis Conditions, Yields, Properties, and Analysis Results of Thiacarbocyanins Containing N-Alkylthio and N,S-Diakylisothiocarbamido Groups

	Quaternary salt and ortho ester	Ml of pyridine	Refining method	Yield, (% of theory) Technical	Yield, (% of theory) Pure	Appearance	M.p.	Formula	% N Experimental	% N Calculated
3,3'-Diethyl-6,6'-di-(N-allylthiocarbamido-N')-thiacarbocyanin p-toluenesulfonate	I, 1	2	A	-	34.0	Lustrous green prisms	192-196°	$C_{36}H_{40}O_3N_6S_5$	10.75 10.63	10.99
3,3'-Diethyl-6,6'-di-(N-allylthiocarbamido-N')--9-methylthiacarbocyanin bromide	I, 2	2.5	A	-	20.3*	Blue lamellae	208-210°	$C_{30}H_{35}N_6S_4Br.2C_2H_5OH$	10.86 10.85	10.78
3,3',9-Triethyl-6,6'-di-(N-allylthiocarbamido-N')-thiacarbocyanin bromide	I, 3	2	B	57.0	22.8*	Violet prisms	225-228°	$C_{31}H_{37}N_6S_4Br.C_2H_5OH$	11.21 11.36	11.24
3,3'-Diethyl-6,6'-di-(N-allyl-S-ethylisothiocarbamido-N')-thiacarbocyanin perchlorate	II, 1	2.5	A	80.1	55.0	Lustrous blue needles	228°	$C_{33}H_{41}O_4N_6S_4Cl$	11.04 10.84	11.22
3,3'-Diethyl-6,6'-di-(N-allyl-S-ethylisothiocarbamido-N')-9-methylthiacarbocyanin perchlorate	II, 2	2.5	A	-	16.3	Minute steel-blue needles	197°	$C_{34}H_{43}O_4N_6S_4Cl$	10.83 10.91	11.01
3,3',9-Triethyl-6,6'-di-(N-allyl-S-ethylisothiocarbamido-N')-thiacarbocyanin perchlorate	II, 3	2.5	A	-	27.0	Green prisms with a golden luster	156°	$C_{35}H_{45}O_4N_6S_4Cl$	10.61 10.67	10.61
3,3'-Diethyl-6,6'-di-(N-benzylthiocarbamido-N')-thiacarbocyanin p-toluenesulfonate	III, 1	3	B	71.7**	43.7	Dark-green, thin, round leaflets	252°	$C_{44}H_{44}O_3N_6S_5$	9.94 10.06	9.72
3,3'-Diethyl-6,6'-di-(N-benzylthiocarbamido-N')-9-methylthiacarbocyanin bromide	III, 2	3	B	-	38.1***	Golden-brown prisms	201-204°	-	-	-
3,3',9-Triethyl-6,6'-di-(N-benzylthiocarbamido-N')-thiacarbocyanin p-toluenesulfonate	III, 3	3	A	-	38.1	Minute violet prisms	180-185°	$C_{46}H_{48}O_3N_6S_5$	9.32 9.46	9.41
3,3'-Diethyl-6,6'-di-(N-benzyl-S-ethylisothiocarbamido-N')-thiacarbocyanin p-toluenesulfonate	IV, 1	4	A	98.4	47.8	Emerald-green lamellae with a golden luster	201-202°	$C_{48}H_{52}O_3N_6S_5$	9.02 9.20	9.15
3,3'-Diethyl-6,6'-di-(N-benzyl-S-ethylisothiocarbamido-N')-9-methylthiacarbocyanin iodide	IV, 2	3	A	38.2****	-	Light-green needles	191-194°	$C_{42}H_{47}N_6S_4I$	9.45 9.56	9.44
3,3',9-Triethyl-6,6'-di-(N-benzyl-S-ethylisothiocarbamido-N')-thiacarbocyanin iodide	IV, 3	1	A	-	10.0****		176-178°	$C_{43}H_{49}N_6S_4I$	9.40 9.51	9.29

*After conversion into the bromide. **The dye was filtered out after the reaction mixture had cooled and washed with water and ethyl alcohol.
***After conversion into the bromide. ****After conversion into the iodide.

Table 3

Data on the Synthesis and Properties of Thiadicarbocyanins With N-Alkylthio- and N,S-Dialkylisothiocarbamido Groups at the 6,6' Positions of the Benzothiazole Rings

	Initial salt	Ml of pyridine	Refining method	Yield (% of theory) Technical	Yield (% of theory) Pure	Appearance	M.p.	Formula	% N Experimental	% N Calculated
3,3'-Diethyl-6,6'-di-(N-allylthiocarbamido-N')-thiadicarbocyanin p-toluenesulfonate	I	2	B (CH_3OH)	75.9	-	Green crystals	200°	$C_{56}H_{42}F_3N_6S_6$	10.94	10.63
3,3'-Diethyl-6,6'-di-(N-allyl-S-ethylisothiocarbamido-N')-thiadicarbocyanin perchlorate	II	2	A (C_2H_5OH)	74.8	38.7	Dark-green prisms	192°	$C_{35}H_{43}O_4N_6S_4Cl$	10.61 10.70	10.84
3,3'-Diethyl-6,6'-di-(N-benzylthiocarbamido-N')-thiadicarbocyanin p-toluenesulfonate	III	6	A (CH_3OH)	89.6	-	Violet prisms with a metallic luster	212°	-	-	-
3,3'-Diethyl-6,6'-di-(N-benzyl-S-ethylisothiocarbamido-N')-thiadicarbocyanin p-toluenesulfonate	IV	5	A (CH_3OH)	84.5	54.8	Lustrous green prisms	215-218°	$C_{50}H_{54}O_3N_6S_6$	8.80 8.99	8.88

Table 4

Data on the Synthesis and Properties of Thiatricarbocyanins With N-Alkylthio- and N,S-Dialkylisothiocarbamido Groups

	Initial salt	Synthesis method	Refining method	Yield (% of theory) Technical	Yield (% of theory) Pure	Appearance	M.p.	Formula	% S Experimental	% S Calculated
3,3'-Diethyl-6,6'-di-(N-allylthiocarbamido-N')-thiatricarbocyanin p-toluenesulfonate	I	2	A	16.3	-	Bronze prisms with a metallic luster	190° (decomposes at 210-220°)	$C_{40}H_{44}O_3N_6S_5$	19.78	19.62
3,3'-Diethyl-6,6'-di-(N-allyl-S-ethylisothiocarbamido-N')-thiatricarbocyanin perchlorate	II	2	A	40.0	-	Golden-green prisms with a metallic luster	201°	$C_{37}H_{45}O_4N_6S_4Cl$	15.85	16.01
3,3'-Diethyl-6,6'-di-(N-benzylthiocarbamido-N')-thiatricarbocyanin p-toluenesulfonate	III	1	B	87.8	41.4	Golden-green prisms	195° (with decomposition)	$C_{48}H_{48}O_3N_6S_5$	17.34	17.48
3,3'-Diethyl-6,6'-di-(N-benzyl-S-ethylisothiocarbamido-N')-thiatricarbocyanin p-toluenesulfonate	IV	1	A	41.1	32.9	Bronze prisms	176° (with decomposition)	$C_{52}H_{56}O_3N_6S_5$	16.36	16.47

Table 5

Data on the Synthesis and Properties of Thiaisocyanins With N-Alkylthio- and N,S-Dialkylisothiocarbamido Groups at the 6 Position of the Benzothiazole Ring

	Initial quaternary salt	Yield (% of theory) Technical	Yield (% of theory) Pure	Appearance	M.p.	Formula	% N Experimental	% N Calculated
3,1'-Diethyl-6-(N-allylthiocarbamido-N')-thiaisocyanin iodide	I	76.6	43.6	Bright-red needles	233-234°	$C_{25}H_{27}N_4S_2I$	9.40 9.71	9.75
3,1'-Diethyl-6-(N-allyl-S-ethylisothiocarbamido-N')-thiaisocyanin perchlorate	II	64.3	41.8	Bright-red needles	198-200°	$C_{27}H_{31}O_4N_4S_2Cl$	9.94	9.75
3,1'-Diethyl-6-(N-benzylthiocarbamido-N')-thiaisocyanin iodide	III	86.5	49.6	Minute dark-red needles	240°	$C_{29}H_{29}N_4S_2I$	8.78 8.81	8.97
3,1'-Diethyl-6-(N-benzyl-S-ethylisothiocarbamido-N')-thiaisocyanin iodide	IV	52.0	23.0	Orthogonal red prisms	203-204°	$C_{31}H_{33}N_4S_2I$	8.61 8.70	8.59

SUMMARY

1. The 6-N-allyl-and benzylthiocarbamido-N'- and 6-N-allyl- and benzyl-S-ethylisothiocarbamido-N'-2-methylbenzothiazoles have been synthesized, plus several quaternary salts of these bases.

2. In an investigation of the feasibility of combining the properties of an optical and a chemical sensitizer within a single dye molecule 24 new iso-, carbo-, dicarbo-, and tricarbocyanins have been prepared from the foregoing quarternary salts.

3. Like other acylamino derivatives, the absorption maxima of thiacyanins possessing thiocarbamido and S-ethylisothio-carbamido groups at the 6 position are shifted toward the shorter wave lengths, compared to the maxima of the respective amino substitution derivatives.

4. Thiacyanins possessing N-alkylthiocarbamido and N,S-dialkylisothiocarbamido groups are rather effective optical sensitizers. However, the presence of N-alkylthiocarbamido groups does not impart the properties of chemical sensitizers to dyes that contain these groups.

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ac-TETRAHYDRONAPHTHOIC AND ac-TETRAHYDROTHIONAPHTHOIC ACIDS AND THEIR DERIVATIVES

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In their studies of hydrogenated naphthoic acids research workers have concentrated upon aromatic tetrahydronaphthoic and dihydronaphthoic acids, the alicyclic tetrahydronaphthoic acids being investigated only in passing, while dealing with other problems, and the information we have on them is extremely limited.

The present research has had as its objective the securing of precise data on the methods of synthesis and the properties of the ac-tetrahydronaphthoic acids themselves and of their derivatives. Moreover, we were also interested in the ac-tetrahydrothionaphthoic acids, which are not described in the literature, in connection with other research of ours.

The method of synthesizing ac-tetrahydronaphthoic acid used most frequently is the reduction of α- and β-naphthoic acids by sodium amalgam [1,2] or by sodium with isoamyl [3] or ethyl alcohol [4]. We employed the method of reduction by sodium with isoamyl alcohol, modifying the quantities of reagents used and the method of processing the substances specified in the literature. The ac-α- and ac-β-tetrahydronaphthoic acids thus synthesized contain no trace of dihydronaphthoic acids (test with bromine water), and their yields ranged from 67 to 70%. The literature contains only brief references to the simplest derivatives of ac-tetrahydronaphthoic acids; Bayer [1], for instance, produced ac-α-tetrahydronaphthoyl chloride by reacting the acid with phosphorus pentachloride, but did not isolate it in the pure state; Derrick and Kamm [2] mention ac-β-tetrahydronaphthoyl chloride but do not give its physical constants, and so forth.

We prepared the ac-tetrahydronaphthoyl chlorides required for our subsequent investigations by reacting the acids with thionyl chloride and then refining the product by distillation in vacuo; we used the acid chlorides to prepare amides of the acids and found that ac-α-tetrahydronaphthamide's melting point is 168°, rather than 116° as stated by Bayer.

The ac-tetrahydronaphthoic acids are readily produced by reacting the chlorides of the respective carboxylic acids with potassium hydrosulfide; they are nearly colorless liquids that distil in vacuo and have a disagreeable odor. We also synthesized the ethyl esters and some alkylaminoalkyl esters of the ac-tetrahydronaphthoic acids and their thio analogs.

EXPERIMENTAL

I. Derivatives of ac-α-Tetrahydronaphthoic Acid

ac-α-Tetrahydronaphthoic acid. A solution of 60 g of α-naphthoic acid in 1200 ml of absolute isoamyl alcohol was heated to boiling, and then 100 to 150 ml of metallic sodium was gradually added so as to keep the alcohol boiling gently. The reaction was carried out in a two-liter flask fitted with a three-elbow adapter and a reflux condenser.

After all the sodium had dissolved, 100 ml of water was added, and the isoamyl alcohol was driven off with steam. The aqueous alkaline solution was extracted with ether to remove tarry substances and then acidulated with dilute hydrochloric acid (1:1). The ac-α-tetrahydronaphthoic acid was extracted with ether, the ether driven off, and the residue recrystallized twice from petroleum ether. This yielded 40 g of ac-α-tetrahydronaphthoic acid with a m.p. of 81-83°. The yield was 67% of the theoretical.

ac-α-Tetrahydronaphthoyl chloride. 14 g of ac-α-tetrahydronaphthoic acid was heated for 4 hours with 32 g of thionyl chloride. The excess thionyl chloride was driven off, and the residue distilled in vacuo. Double distillation yielded 14 g of a yellowish liquid with a b.p. of 142.5-143° at 18 mm. The yield was 91% of the theoretical.

0.2482 g. subst.: 0.1872 g AgCl. 0.2069 g. subst.: 0.1562 g AgCl. Found %: Cl 18.66, 18.67. $C_{11}H_{11}OCl$. Calculated %: Cl 18.30.

ac-α-Tetrahydronaphthamide. This was prepared by reacting ac-α-tetrahydronaphthoyl chloride with an aqueous solution of ammonia. Double recrystallization from aqueous methanol yielded the amide with a m.p. of 168°; it crystallized as elongated needles.

3.198 mg subst.: 8.850 mg CO_2; 2.146 mg H_2O. 3.125 mg subst.: 8.637 mg CO_2; 2.142 mg H_2O. 6.158 mg subst.: 0.433 ml N_2 (29.5°, 724.5 mm). 6.730 mg subst.: 0.483 ml N_2 (29.5°, 720.5 mm). Found %: C 75.47, 75.38; H 7.51, 7.67; N 7.55, 7.67; $C_{11}H_{13}ON$. Calculated %: C 75.49; H 7.43; N 8.00.

Dimethylaminoethyl ester (hydrochloride). 3.9 g (0.02 mole) of ac-α-tetrahydronaphthoylchloride was dissolved in 20 ml of absolute benzene, 1.7 g (0.02 mole) of dimethylaminoethanol were added to the solution, and the mixture was heated to boiling for 6 hours. The benzene was driven off, and the residue triturated with absolute ether until it solidified. This yielded 4.4 g of a colorless hygroscopic substance with a m.p. of 110-112.5°. Double recrystallization from absolute benzene did not raise the melting point. The yield was about 72% of the theoretical.

The hydrochloride of the dimethylaminoethyl ester of ac-α-tetrahydronaphthoic acid is a colorless hygroscopic substance that is readily soluble in water, alcohol, and chloroform, and when heated in benzene. It is insoluble in ether.

5.513 mg subst.: 0.232 ml N_2 (17°, 730.5 mm). Found %: N 4.76. $C_{15}H_{21}O_2N \cdot HCl$. Calculated %: N 4.93.

Diethylaminoethyl ester (hydrochloride).[1]
A mixture of 2.5 g of ac-α-tetrahydronaphthoyl chloride, 1.5 g of diethylaminoethanol, and 30 ml of absolute benzene was heated to boiling for 3-4 hours. The hydrochloride of the diethylaminoethyl ester of ac-α-tetrahydronaphthoic acid crystallized out as the mixture cooled, yielding 2.6 g of a substance with a m.p. of 115-117°. A single recrystallization from absolute benzene to which chloroform had been added yielded 2.2 g of a substance with a m.p. of 139.5-140°. The yield was about 55% of the theoretical.

The hydrochloride of the diethylaminoethyl ester of ac-α-tetrahydronaphthoic acid is a colorless, slightly hygroscopic substance, soluble in water, alcohol, and chloroform, and when heated in benzene.

[1]) Synthesized previously, cf [5].

6.537 mg substance: 0.256 ml N_2 (29.5°, 725.0 mm). Found %: N 4.31. $C_{17}H_{25}O_2N \cdot HCl$. Calculated %: N 4.50.

Isopropylaminoethyl ester (hydrochloride). 1.95 g (0.01 mole) of ac-α-tetrahydronaphthoyl chloride was dissolved in 10 ml of anhydrous chloroform, and a solution of 1 g (0.01 mole) of isopropylaminoethanol in chloroform saturated with anhydrous hydrogen chloride was added. The mixture was then heated to 50-55° for 24 hours. When the reaction was finished, the chloroform was driven off in vacuo, and the residue triturated with absolute ether until it solidified. This yielded 2.2 g of a white substance with a m.p. of 107-114°. Double recrystallization from absolute benzene to which absolute ether had been added yielded 2 g of a substance with a m.p. of approximately 119-121°. The yield was 67% of the theoretical. The hydrochloride is soluble in water and alcohol and, when heated, in benzene.

6.999 mg substance: 0.294 ml N_2 (18.0°, 737.0 mm). Found %: N 4.99. $C_{18}H_{29}O_2N \cdot HCl$. Calculated %: N 4.71.

γ-Chloropropyl ester. 17.6 g (0.1 mole) of ac-α-tetrahydronaphthoic acid was dissolved in methanol, and an alcoholic solution of KOH (phenolphthalein test) was added to the solution, after which the alcohol was driven off completely in vacuo. The resulting potassium salt of ac-α-tetrahydronaphthoic acid was heated to 100° for 20 hours with 50 g of trimethylene chlorobromide, after which the reaction mixture was poured into water. The lower layer was separated, washed with water, and desiccated with $CaCl_2$. Double distillation in vacuo yielded 18.5 g of a light-yellow liquid with a b.p. of 164-165° at 4 mm. The yield was about 73% of theoretical.

0.2166 g substance: 0.1188 g AgCl. 0.2277 g substance: 0.1260 g AgCl. Found %: Cl 13.57, 13.69. $C_{14}H_{17}O_2Cl$. Calculated %: Cl 15.06.

γ-Diethylaminopropyl ester (hydrochloride). A mixture of 2.6 g (0.01 mole) of the γ-chloropropyl ester of ac-α-tetrahydronaphthoic acid, 7.0 (0.01 mole) of diethylamine, and 0.2 g of NaI was heated to boiling for 16 hours, after which the reaction mixture was poured into water and extracted with ether. The ether solution was washed with water and desiccated with Na_2SO_4. Then the ether and the diethylamine were driven off by heating in vacuo to 100°. The residue was dissolved in absolute ether, the hydrochloride being thrown down by adding an ether solution of hydrogen chloride.

The hydrochloride of the γ-diethylaminopropyl ester of ac-α-tetrahydronaphthoic acid was recrystallized twice from a mixture of absolute benzene and absolute ether. This yielded 0.8 g of a substance with a m.p. of 107-108.5°. The yield was about 24% of the theoretical. The substance is soluble in water and alcohol and, when heated, in benzene.

7.579 mg substance: 0.276 ml N_2 (16.0°, 747.6 mm). 6.960 mg substance: 0.269 ml N_2 (16.0°, 742.6 mm). Found %: N 4.24, 4.46. $C_{18}H_{27}O_2N \cdot HCl$. Calculated %: 4.30.

II. ac-α-Tetrahydrothionaphthoic Acid and Its Derivatives

ac-α-Tetrahydrothionaphthoic acid. 9.5 g of potassium hydroxide (90% alkali) was dissolved in 50 ml of absolute alcohol. The solution was chilled to minus 5 to 10° and then saturated with hydrogen sulfide as determined by its gain in weight (about 7 g). A solution of 14.5 g of ac-α-tetrahydronaphthoyl chloride in 10 ml of absolute benzene was gradually added, with mechanical stirring, to the resulting solution of potassium hydrosulfide. The temperature of the reaction mass did not exceed -2°. Stirring was continued for 15 minutes, after which the precipitated KCl was filtered out and the filtrate evaporated in vacuo until a viscous mass was produced. Trituration with absolute ether yielded 13 g of the potassium salt of ac-α-tetrahydrothionaphthoic acid. The yield was about 76% of the theoretical.

The potassium salt was dissolved in water and acidulated with dilute hydrochloric acid, the oil that settled out being extracted with ether. The ether solution was washed with water and desiccated with Na_2SO_4, after which the ether was driven off, and the residue distilled twice in vacuo.

ac-α-Tetrahydrothionaphthoic acid is a colorless liquid with a b.p. of 142-143° at 7 mm. It must be kept in a sealed ampoule, turning turbid when exposed to air.

0.1900 g subst.: 0.222 g $BaSO_4$. Found %: S 16.04. $C_{11}H_{12}OS$. Calculated %: S 16.66.

Ethyl ester of ac-α-tetrahydrothionaphthoic acid. 3.0 g of the potassium salt of ac-α-tetrahydrothionaphthoic acid was heated on a water bath for 2.5 hours with 30 g of C_2H_5I. Then water was added, the heavy organic layer was separated, and the excess C_2H_5I was driven off. Distillation in vacuo yielded 2.0 g of a colorless liquid with a b.p. of 152-153° at 7 mm. The yield was about 70% of the theoretical.

0.1972 g substance: 0.2080 g $BaSO_4$. 0.2668 g substance: 0.2822 g $BaSO_4$. Found %: S 14.48, 14.52. $C_{13}H_{16}OS$. Calculated %: S 14.54.

Diethylaminoethyl ester (hydrochloride) of ac-α-tetrahydrothionaphthoic acid. 2.6 grams (0.01 mole + an excess of 0.3 g) of the potassium salt of ac-α-tetrahydrothionaphthoic acid was dissolved in 15 ml of absolute ether, 1.35 g (0.01 mole) of freshly distilled diethylaminoethyl chloride were added, and the mixture was heated to 50-60° for 5 hours. The precipitated KCl was filtered out, and the filtrate was evaporated in vacuo until nearly all the alcohol had been driven off. Water was added to the residue, and the alkamino ester was extracted with ether. The ether solution was washed with water and desiccated with Na_2SO_4. The hydrochloride was thrown down by carefully adding an ether solution of HCl. This yielded 3.2 g of a substance with a m.p. of 118-128°. Then the hydrochloride was recrystallized twice from absolute benzene to which chloroform had been added. This yielded 2.6 g of a colorless substance with a m.p. of 142-144°. The yield was about 79% of the theoretical.

The hydrochloride of the diethylaminoethyl ester of ac-α-tetrahydrothionaphthoic acid consists of cubes that are readily soluble in water, alcohol, and chloroform, and, when heated, in benzene. They are insoluble in ether.

0.1980 g substance: 0.1410 g $BaSO_4$. Found %: S 9.78. $C_{17}H_{25}ONS \cdot HCl$. Calculated %: S 9.77.

III. Derivatives of ac-β-tetrahydronaphthoic Acid

ac-β-Tetrahydronaphthoic acid. The method used for the synthesis of ac-β-tetrahydronaphthoic acid was similar to that used in preparing the ac-α-tetrahydronaphthoic acid, the sole difference being that the β-naphthoic acid was added to the reaction mixture gradually, as hydrogenation progressed, inasmuch as the sodium salt of β-naphthoic acid is very slightly soluble in isoamyl alcohol.

A solution of 10 g of β-naphthoic acid in 1200 ml of isoamyl alcohol was placed in a two-liter flask, the solution was heated to boiling, and 20 g of metallic sodium was gradually added, precipitating the jellylike sodium salt of β-naphthoic acid, which disappeared as hydrogenation progressed, after which 10 more grams of the naphthoic acid and 20 g of sodium were added, and so forth. A total of 40 g of β-naphthoic acid and 100 g of sodium was placed in reaction in this manner. When the reaction was finished, water was added and the isoamyl alcohol

was driven off with steam, the remaining aqueous alkaline solution being acidulated with hydrochloric acid. The ac-β-tetrahydronaphthoic acid that settled out as an oil soon solidified. The yield was 34 g. The m.p. was 94° after recrystallization from petroleum ether.

Ethyl ester. 5 grams of ac-β-tetrahydronaphthoic acid was heated for 2.5 hours with 40 ml of absolute alcohol and 10 drops of concentrated H_2SO_4. When the reaction was finished, the excess alcohol was driven off, water was added, and the mixture was extracted with ether. The ether solution was washed with water and a soda solution and desiccated with Na_2SO_4. After double distillation in vacuo the ethyl ester of ac-β-tetrahydronaphthoic acid was a colorless, fragrant liquid with a b.p. of 136-137° at 6 mm. The yield totaled 4.5 g of the substance, or about 78% of the theoretical.

3.767 mg substance: 10.544 mg CO_2; 2.592 mg H_2O. Found %: C 76.34; H 7.70. $C_{13}H_{16}O_2$. Calculated %: C 76.47; H 7.84.

Acid chloride. 25 grams of ac-β-tetrahydronaphthoic acid was heated for 4 hours with 60 g of $SOCl_2$. When the reaction was finished, the excess thionyl chloride was driven off, and the acid chloride twice distilled in vacuo. This yielded 27 g of a yellow-greenish liquid with a b.p. of 141° at 8 mm. The yield was about 97% of the theoretical.

0.2122 g substance: 0.1545 g AgCl. 0.2160 g substance: 0.1590 g AgCl. Found %: Cl 18.01, 18.21. $C_{11}H_{11}OCl$. Calculated %: Cl 18.30.

Amide.[1] This was prepared by reacting the ac-β-tetrahydronaphthoyl chloride with a concentrated aqueous solution of NH_3. After double recrystallization from aqueous methanol the ac-β-tetrahydronaphthamide consisted of colorless needles with a m.p. of 136-137°, readily soluble in methanol.

6.023 mg substance: 0.446 ml N_2 (27.5°, 729.0 mm). Found %: N 8.06. $C_{11}H_{13}ON$. Calculated %: N 8.00.

Dimethylaminoethyl ester (hydrochloride). A mixture of 1.95 g (0.01 mole) of ac-β-tetrahydronaphthoyl chloride, 0.8 g (0.01 mole) of dimethylaminoethylethanol, and 30 ml of absolute benzene was heated to boiling for 5 hours. Absolute ether was added after it had cooled, the resultant precipitate being filtered out. This yielded 2.4 g of a substance with a m.p. of 110-114°, the yield being about 86% of the theoretical. Repeated recrystallization from a benzene-chloroform mixture yielded a colorless, slightly hygroscopic substance with a m.p. of 125-126°, which was readily soluble in water, alcohol, and chloroform, and, when heated, in benzene.

7.443 mg substance: 0.310 ml N_2 (17.0°, 745.0 mm). Found %: N 4.81. $C_{15}H_{21}O_2N \cdot HCl$. Calculated %: N 4.93.

Diethylaminoethyl ester (hydrochloride). 3.9 grams of ac-β-tetrahydronaphthoyl chloride was heated together with 2.35 g of diethylaminoethanol and 30 ml of absolute benzene. A precipitate settled out as the solution cooled. This yielded 6.0 g of a substance with a m.p. of 114-117°, the yield being about 96% of the theoretical. Triple recrystallization from a mixture of absolute benzene and chloroform yielded the hydrochloride of the diethylaminoethyl ester of ac-β-tetrahydronaphthoic acid as a colorless, hygroscopic substance with a m.p. of 122.5-123.5°, which was readily soluble in water, alcohol, and chloroform, and when heated, in benzene.

5.558 mg substance: 0.217 ml N_2 (32°, 731 mm). 6.783 mg substance: 0.258 ml N_2 (28.0°, 727 mm). Found %: N 4.17, 4.12. $C_{17}H_{25}O_2N \cdot HCl$. Calculated %: N 4.50

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[1] Also synthesized by C. Derrick and O. Kamm [2], with a m.p. of 137°.

Isopropylaminoethyl ester (hydrochloride). A solution of 2.1 g (0.01 mole + an excess of 0.15 g) of ac-β-tetrahydronaphthoyl chloride in 10 ml of $CHCl_3$ was mixed with a solution of 1 g (0.01 mole) of isopropylaminoethanol in chloroform saturated with anhydrous HCl. The mixture was heated to 50-60° for 24 hours, after which the chloroform was driven off in vacuo and the residue triturated with absolute ether until it solidified. This yielded 2.2 g of a substance with a m.p. of 132-137°, or about 73% of the theoretical. Several recrystallizations from absolute benzene to which chloroform had been added yielded a substance with a m.p. of 151.5-152.5° as minute needles soluble in water and chloroform.

7.756 mg substance: 0.326 ml N_2 (20.5°, 743.0 mm). Found %: N. 4.78. $C_{18}H_{23}O_2N \cdot HCl$. Calculated %: N 4.71.

γ-Chloropropyl ester. 8.8 grams (0.05 mole) of ac-β-tetrahydronaphthoic acid was dissolved in methanol and neutralized with an alcoholic solution of KOH. The alcohol was driven off in vacuo, and the residual potassium salt of ac-β-tetrahydronaphthoic acid was heated with 50 g of trimethylene chlorobromide to 100° for 20 hours. Then water was added, and the lower layer was separated, washed with water, and distilled in vacuo. This yielded 10.0 g of a light-yellow liquid with a b.p. of 164-165° at 6 mm, or about 80% of the theoretical.

0.3547 g substance: 0.1944 g AgCl. 0.2541 g substance: 0.1414 g AgCl. Found %: Cl 13.56, 13.76. $C_{14}H_{17}O_2Cl$. Calculated %: Cl 14.06.

γ-Diethylaminopropyl ester (hydrochloride). A mixture of 2.6 g (0.01 mole) of the γ-chloropropyl ester of ac-β-tetrahydronaphthoic acid, 7 g (0.1 mole) of diethyl amine, and 0.2 g of NaI was heated to boiling for 16 hours. The reaction mixture was then treated with water and extracted with ether. Procedures analogous to those used in synthesizing the corresponding alkylamino ester of ac-α-tetrahydronaphthoic acid yielded 1.4 g of a substance with a m.p. of 124-125.5°. The yield was about 42% of the theoretical. Double recrystallization from absolute benzene yielded a colorless substance with a m.p. of 125.5-126.5°, soluble in water and alcohol.

6.012 mg substance: 0.233 ml N_2 (17°, 730.5 mm). Found %: N 4.39. $C_{18}H_{27}O_2N \cdot HCl$. Calculated %: N 4.30.

IV. ac-β-Tetrahydrothionaphthoic Acid and Its Derivatives

ac-β-Tetrahydrothionaphthoic acid. This was synthesized by a method resembling that used for the corresponding α-tetrahydrothionaphthoic acid. The yield of the potassium salt of ac-β-tetrahydrothionaphthoic acid was about 76% of the theoretical. Acidulation of an aqueous solution of the potassium salt yielded ac-β-tetrahydrothionaphthoic acid, a yellowish liquid with a b.p. of 148-150° at 6 mm.

0.2870 g substance: 0.3550 g $BaSO_4$. Found %: S 16.03. $C_{11}H_{12}OS$. Calculated %: S 16.66.

Ethyl ester of ac-β-tetrahydrothionaphthoic acid. This was produced by reacting the potassium salt of ac-β-tetrahydrothionaphthoic acid with C_2H_5I (cf the corresponding ester of the α-acid), the yield being 70%.

The ethyl ester of ac-β-tetrahydrothionaphthoic acid is a colorless liquid with a b.p. of 158° at 6 mm.

0.2388 g substance: 0.2527 g $BaSO_4$. 0.2213 g substance: 0.2340 g $BaSO_4$. Found %: S 14.56, 14.52. $C_{13}H_{16}OS$. Calculated %: S 14.54.

γ-Diethylaminopropyl ester. 2.8 grams (0.01 mole + an excess of 0.5 g) of

the potassium salt of ac-β-tetrahydrothionaphthoic acid was heated together with 1.5 g of freshly distilled diethylaminopropyl chloride and 15 ml of absolute alcohol for 5 hours at 50-55°. The precipitated KCl was filtered out, and the filtrate evaporated in vacuo. The usual processing yielded 2.6 g of the hydrochloride of the alkamino ester with a m.p. of 110-115°, the yield being about 76% of the theoretical. Triple recrystallization from absolute benzene to which absolute ether had been added yielded a substance with a m.p. of 119-121°. Light-yellow leaflets, readily soluble in alcohol and in water, and, when heated, in benzene.

0.1520 g substance: 0.1077 g $BaSO_4$. 0.1380 g substance: 0.0967 g $BaSO_4$. Found %: S 9.73, 9.62. $C_{18}H_{27}ONS \cdot HCl$. Calculated %: S 9.37.

SUMMARY

1. The simplest derivatives of ac-tetrahydronaphthoic acids and their alkylaminoalkyl esters have been synthesized. It has been found that the melting point of ac-α-tetrahydronaphthamide is 168°, and not 116° as stated in the literature.

2. ac-Tetrahydrothionaphthoic acids and their ethyl and alkylaminoalkyl esters have been synthesized.

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NAPHTHALENE ANESTHETICS

VII. MONOALKYLAMINOALKYL ESTERS OF SOME NAPHTHALENECARBOXYLIC ACIDS

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The monoalkylaminoalkyl esters of aromatic acids have attracted considerable attention during the past ten or fifteen years as anesthetics of a new type. The dialkylaminoalkyl esters of 4-amino-1-naphthoic acid, first synthesized by one of the present authors together with V. V. Nesvalba [1], proved to be anesthetics of high quality, so that we thought it advisable to prepare the monoalkylaminoalkyl esters of 4-amino-1-naphthoic acids and of various other naphthalene acids by way of pursuing our previous research.

We prepared the initial monoalkylaminoethanols ($HOCH_2CH_2NHR$), with normal alkyl radicals attached to the nitrogen atom, by reacting aminoethanol with alkyl halides [2], those with branched radicals attached to the nitrogen atom being prepared by hydrogenating a mixture of aminoethanol and aliphatic ketones (acetone or methyl ethyl ketone) catalytically [3].

Before condensing the chlorides of naphthalene acids with alkylamino alcohols, we dissolved the latter in chloroform saturated with hydrogen chloride, placing them in the reaction in that form, in order to avoid acylation of the secondary amino group [4]. This method was used to synthesize the monopropyl-, monoisopropyl-, monobutyl-, monoisobutyl-, and monoheptylaminoethyl esters of 4-nitro-1-naphthoic acid, the monobutylaminoethyl ester of 5-nitro-1-naphthoic acid, and the monobutyl- and monoisobutylaminoethyl esters of β-(naphthyl-1)-acrylic acid.

In all these esters of 4(5)-nitro-1-naphthoic acids, the nitro group was reduced catalytically. The use of Raney nickel as the catalyst (which we frequently employed in the past in analogous cases [5]) involved no difficulty in the reduction of the esters of 4-nitro-1-naphthoic acid. The reaction was carried out at atmospheric pressure and a temperature of 25-30°, sometimes 40°. Methanol was used as the solvent.

The hydrochlorides of the monoalkylaminoethyl esters of 4-amino-1-naphthoic acid are faintly colored crystalline substances whose melting points are much higher than those of the hydrochlorides of the corresponding esters of 4-nitro-1-naphthoic acid.

The use of Raney nickel in reducing the monobutylaminoethyl ester of 5-nitro-1-naphthoic acid under the conditions specified results in failure: hydrogen was absorbed very slowly and the quantity absorbed totaled only 70% of the theoretical, so that we were forced to employ another catalyst. Using palladium black in this reduction proved to be entirely satisfactory.

Monoalkylaminoalkyl Esters of 4-Nitro-(Amino)-1-Naphthoic Acids

Propylaminoethyl ester of 4-nitro-1-naphthoic acid (hydrochloride). 5.1 ml of chloroform, saturated with hydrogen chloride and containing 1.5 g of n-propylaminoethanol, was added to 3.25 g of 4-nitronaphthoyl chloride dissolved in 5 ml of chloroform. The reaction mixture was refluxed for 24 hours at a water-bath temperature of 55-60°. When the reaction was finished, the chloroform was driven off in vacuo, and the remaining dark-brown oily substance was washed with absolute ether to solidify it, after which it was recrystallized from absolute ethyl alcohol. The

first crystallization yielded 1 g of a substance with a m.p. of 171-174°. The second recrystallization raised the m.p. to 173-174°.

The hydrochloride of the propylaminoethyl ester of the 4-nitronaphthoic acid is freely soluble in ethyl acetate, benzene, and petroleum ether.

6.995 mg substance: 0.522 ml N_2 (22°, 730 mm). Found %: N 8.30. $C_{16}H_{18}O_4N_2 \cdot HCl$. Calculated %: N 8.27.

Propylaminoethyl ester of 4-amino-1-naphthoic acid (hydrochloride). 0.3 gram of the hydrochloride of the propylaminoethyl ester of 4-nitronaphthoic acid was dissolved in methanol and then agitated in hydrogen with 0.12 g of Raney's nickel catalyst at 25-30° and atmospheric pressure. The theoretical amount of hydrogen was absorbed in 3 hours, after which the catalyst was filtered out, the solvent was driven off in vacuo, and the residue was crystallized from 96% ethyl alcohol. This yielded 0.15 g of the hydrochloride of the propylaminoethyl ester of 4-aminonaphthoic acid with a m.p. of 205-206°. Several recrystallizations yielded the substance as faintly colored crystals with a m.p. of 208-208.5°.

5.342 mg substance: 0.431 ml N_2 (21.5°, 731 mm). 4.777 mg substance: 0.386 ml N_2 (19.5°, 737.5 mm). Found %: N 9.00, 9.15. $C_{16}H_{20}O_2N_2 \cdot HCl$. Calculated %: N 9.07.

Isopropylaminoethyl ester of 4-nitro-1-naphthoic acid (hydrochloride). 2.2 grams of 4-nitronaphthoyl chloride dissolved in chloroform and 1 g of isopropylaminoethanol dissolved in 2.5 ml of chloroform previously saturated with hydrogen chloride were placed in a round-bottomed flask fitted with a reflux condenser. The reaction mixture was refluxed for 24 hours on a water bath at 50-55°, after which the chloroform was driven off in vacuo, the unreacted 4-nitronaphthoyl chloride eliminated, and the residual oily substance treated with absolute ether until it turned into a solid, when it was crystallized from absolute ethyl alcohol until its melting point was a constant. The hydrochloride of the isopropylaminoethyl ester of 4-nitronaphthoic acid is a colorless crystalline substance with a m.p. of 175-176°.

4.635 mg substance: 0.345 ml N_2 (26°, 736.6 mm). 4.795 mg substance: 0.336 ml N_2 (20°, 741 mm). Found %: N 8.23, 8.04. $C_{16}H_{18}O_4N_2 \cdot HCl$. Calculated %: N 8.27.

Isopropylaminoethyl ester of 4-amino-1-naphthoic acid (hydrochloride). 0.3 gram of the hydrochloride of the isopropylaminoethyl ester of 4-nitro-1-naphthoic acid was dissolved in methanol and then agitated in hydrogen with 0.12 g of Raney's nickel catalyst at room temperature and atmospheric pressure. The theoretical amount of hydrogen (65 ml) was absorbed in 3.5 hours, after which the catalyst was filtered out and the solvent driven off in vacuo. The remaining dark, oily product was allowed to stand beneath a layer of absolute ether until it hardened. The resultant substance was crystallized from absolute ethyl alcohol and then recrystallized several times, yielding the hydrochloride of the isopropylaminoethyl ester of 4-aminonaphthoic acid as a colorless crystalline substance with a m.p. of 200.5-201°. The hydrochloride of the alkamino ester is readily soluble in methanol and acetone; it dissolves when heated in chloroform and ethyl alcohol, but is insoluble in benzene, carbon tetrachloride, or petroleum ether. Its solubility in water is 1:20.

3.923 mg substance: 0.329 ml N_2 (23.5°, 730 mm). 5.017 mg substance: 0.390 ml N_2 (17.0°, 745 mm). Found %: N 9.27, 8.98. $C_{16}H_{20}O_2N_2 \cdot HCl$. Calculated %: N 9.07.

Butylaminoethyl ester of 4-nitro-1-naphthoic acid (hydrochloride). 1.1 grams of n-butylaminoethanol, dissolved in 3 ml of chloroform saturated with hydrogen chloride, and 2 g of 4-nitronaphthoyl chloride were placed in a round-bottomed flask fitted with a reflux condenser, and the reaction mixture was heated for 24 hours to 50-55° on a water bath, after which the chloroform was driven off in

vacuo. The oily, light-brown substance produced was allowed to stand for some time with absolute ether, which extracted the unreacted 4-nitronaphthoyl chloride. The substance that did not dissolve was filtered out, dried in vacuo, and recrystallized from absolute ethyl alcohol. This yielded 1.25 g of the nitro ester's hydrochloride with a m.p. of 161-162°. Numerous recrystallizations raised the m.p. of the hydrochloride of the butylaminoethyl ester to 162.5-163°. The hydrochloride is soluble in water, methanol, and ethyl alcohol, and sparingly soluble in ethyl acetate and acetone. Crystallization from chloroform may be successfully used instead of crystallization from ethyl alcohol.

7.920 mg substance: 0.545 ml N_2 (16.5°, 727.5 mm). Found %: N 7.77. $C_{17}H_{20}O_4N_2 \cdot HCl$. Calculated %: N 7.94.

Butylaminoethyl ester of 4-amino-1-naphthoic acid (hydrochloride). 1.2 grams of the hydrochloride of the butylaminoethyl ester of 4-nitronaphthoic acid was dissolved in methanol, 0.48 g of Raney's nickel catalyst suspended in methanol was added to the solution, and the mixture was agitated in hydrogen at atmospheric pressure and a temperature of 25-30°. The theoretical amount of hydrogen (228 ml) was absorbed within 1.5 hours, after which the catalyst was filtered out and the solvent driven off in vacuo. The slightly colored substance left after the solvent had been driven off was washed with ether, dried in vacuo, and crystallized from 96% ethyl alcohol. The first crystallization yielded 0.5 g of the hydrochloride with a m.p. of 205-206°. Triple recrystallization from ethyl alcohol yielded a substance with the constant m.p. of 206-207°.

The hydrochloride of the butylaminoethyl ester of 4-aminonaphthoic acid consists of faintly colored needles that are sparingly soluble in acetone, petroleum ether, and chloroform, and soluble when heated in methanol and ethyl alcohol. The solubility of the hydrochloride in water is negligible; when a one per cent aqueous solution is allowed to stand for a long time, the substance crystallizes out as lustrous large needles. It is not hydrolyzed by boiling.

5.159 mg substance: 0.410 ml N_2 (22°, 733.5 mm). 5.332 mg substance: 0.414 ml N_2 (20°, 743 mm). Found %: N 8.87, 8.84. $C_{17}H_{22}O_2N_2 \cdot HCl$. Calculated %: N 8.69.

Isobutylaminoethyl ester of 4-nitro-1-naphthoic acid (hydrochloride). 3.3 grams of 4-nitronaphthoyl chloride was dissolved in 15 ml of anhydrous chloroform, and 4.1 ml of chloroform saturated with hydrogen chloride and containing 1.8 g of sec-butylaminoethanol was added to the solution. The reaction mixture was refluxed for 24 hours on a water bath at 55-60°. After the chloroform had been driven off in vacuo, there was left 3.8 g of an oily product, which was chilled and then thoroughly triturated with absolute ether until a solid substance was formed. A series of successive crystallizations from absolute ethyl alcohol yielded a colorless crystalline substance with a m.p. of 152-153°. The hydrochloride of the isobutylaminoethyl ester of 4-nitronaphthoic acid crystallizes from acetone as minute colorless, lustrous needles. The hydrochloride is freely soluble in methanol and ethyl alcohol.

3.943 mg substance: 0.275 ml N_2 (17.5°, 748 mm). Found %: N 8.07. $C_{17}H_{20}O_4N_2 \cdot HCl$. Calculated %: N 7.94.

Isobutylaminoethyl ester of 4-amino-1-naphthoic acid (hydrochloride). 1.2 grams of the isobutylaminoethyl ester of 4-nitronaphthoic acid was agitated together with 0.48 g of Raney's nickel catalyst in a methanol solution at 30-40° in an atmosphere of hydrogen. The theoretical amount of hydrogen (230 ml) was absorbed within 1 hour, after which the catalyst was filtered out and the solvent driven off in vacuo. Driving off the solvent left behind a faintly colored substance. Repeated recrystallization yielded the hydrochloride of the isobutylaminoethyl ester of 4-nitronaphthoic acid as lustrous, faintly colored crystals with a m.p. of 181-182°.

The hydrochloride was soluble when heated in absolute and aqueous ethyl alcohol, and is insoluble in acetone, chloroform, or ethyl acetate. Its solubility in water is 1:50.

4.604 mg substance: 0.352 ml N_2 (18.5°, 736.0 mm). 2.774 mg substance: 0.254 ml N_2 (18.5°, 724.0 mm). Found %: N 8.67, 8.81. $C_{17}H_{22}O_2N_2 \cdot HCl$. Calc.%: N 8.69.

Heptylaminoethyl ester of 4-nitro-1-naphthoic acid (hydrochloride). 1 gram of 4-nitronaphthoyl chloride, dissolved in 5 ml of chloroform saturated with hydrogen chloride and containing 0.73 g of heptylaminoethanol, was placed in a round-bottomed flask fitted with a reflux condenser. The reaction mass was heated for 24 hours on a water bath at 50-55°, after which the chloroform was driven off in vacuo and the residual substance was washed with absolute ether to eliminate any traces of the unreacted 4-nitronaphthoyl chloride. The oily substance turned into a solid, which was filtered out and crystallized from absolute ethyl alcohol. This yielded 0.55 g (35% yield) of a substance with a m.p. of 147-149°.

The hydrochloride of the heptylaminoethyl ester of 4-nitronaphthoic acid is a colorless crystalline substance with a m.p. of 148-149° that is freely soluble in methanol and chloroform, and sparingly soluble in petroleum ether, acetone, and ethyl alcohol.

4.731 mg substance: 0.313 ml N_2 (19.5°, 717.5 mm). Found %: N 7.09. $C_{20}H_{28}O_4N_2 \cdot HCl$. Calculated %: N 7.28.

Heptylaminoethyl ester of 4-amino-1-naphthoic acid (hydrochloride). 0.4 gram of the hydrochloride of the heptylaminoethyl ester of 4-nitronaphthoic acid was dissolved in methanol and then agitated with 0.16 g of Raney's nickel catalyst in hydrogen at atmospheric pressure and at a temperature of 25-30°. The theoretical amount of hydrogen (70 ml) was absorbed within 1 hour, after which the catalyst was filtered out and the solvent driven off in vacuo. The residual substance was recrystallized from 96% ethyl alcohol, yielding 0.3 g of the alkamino ester's hydrochloride (with a m.p. of 191-192°), representing 80% of the theoretical yield. The hydrochloride of the heptylaminoethyl ester of 4-aminonaphthoic acid is insoluble in the ordinary organic solvents at room temperature; though it does dissolve when heated in methanol and ethyl alcohol, it is insoluble in chloroform, petroleum ether, or benzene. The solubility of the hydrochloride of the heptylaminoethyl ester of 4-aminonaphthoic acid in water is extremely low, 0.1 g of the substance dissolving in 35 ml of water.

5.683 mg substance: 0.382 ml N_2 (19.5°, 739 mm). 6.325 mg substance: 0.431 ml N_2 (19.0°, 732 mm). Found %: N 7.63, 7.67. $C_{20}H_{28}O_2N_2 \cdot HCl$. Calculated %: N 7.68.

Monobutylaminoethyl Esters of 5-Nitro-(or Amino)-1-naphthoic Acids

Butylaminoethyl ester of 5-nitro-1-naphthoic acid (hydrochloride)[1]. 1.3 grams of 5-nitronaphthoyl chloride was dissolved in chloroform, and 0.6 g of butylaminoethanol in chloroform saturated while chilled with hydrogen chloride was added. Then the reaction mixture was heated to 55-60° for 24 hours, after which the chloroform was driven off in vacuo. The resultant pasty substance was triturated with absolute ether, yielding a nearly colorless powder with a m.p. of 188-190°. Two recrystallizations from absolute ethyl alcohol yielded a crystalline substance with a m.p. of 197-198°.

The hydrochloride of the butylaminoethyl ester of 5-nitronaphthoic acid is freely soluble in methanol, dissolving when heated in chloroform, ethyl alcohol, and acetone, though not dissolving in petroleum ether.

6.975 mg substance: 0.492 ml N_2 (24°, 737 mm). Found %: N 7.86. $C_{17}H_{20}O_4N_2 \cdot HCl$. Calculated %: N 7.94.

[1]) See next page.

Butylaminoethyl ester of 5-amino-1-naphthoic acid (hydrochloride). 0.7 gram of the hydrochloride of the butylaminoethyl ester of 5-nitronaphthoic acid was dissolved in methanol, and the solution was added to previously reduced palladium black.

The amount of hydrogen theoretically required to reduce the nitro group (135 ml) was absorbed within 20 minutes. After the solvent had been driven off in vacuo, we secured a faintly colored substance with a m.p. of 217-218°. Crystallization from absolute ethanol yielded 0.2 g of a substance with a m.p. of 219-220° (0.3 g of a substance with a m.p. of 217-220° was recovered from the mother liquor).

The hydrochloride of the buytlaminoethyl ester of 5-aminonaphthoic acid is a colorless crystalline substance that is sparingly soluble in ordinary organic solvents at room temperature, soluble when heated in methanol and ethyl alcohol, and insoluble in chloroform, petroleum ether, and carbon tetrachloride.

3.351 mg substance: 0.264 ml N_2 (22°, 731 mm). 5.099 mg substance: 0.396 ml N_2 (19°, 730 mm). Found %: N 8.77, 8.72. $C_{17}H_{22}O_2N_2 \cdot HCl$. Calculated %: N 8.69.

Isobutylaminoethyl ester of 5-nitro-1-naphthoic acid (hydrochloride). 1.6 grams of 5-nitronaphthoyl chloride was dissolved in chloroform, and 3 ml of chloroform containing 1 g of isobutylaminoethanol and saturated with hydrogen chloride was added to the solution. The reaction mixture was refluxed on a water bath at 55-60° in a flask fitted with a reflux condenser and a calcium chloride tube. An abundant colorless precipitate settled out of the solution after 10-12 hours of heating. After heating had continued for 24 hours, the solvent was driven off in vacuo, and the residue was washed with absolute ether. A first crystallization from absolute ethyl alcohol yielded 0.9 g of a substance with a m.p. of 220-221°.

The hydrochloride of the isobutylaminoethyl ester of 5-nitronaphthoic acid is sparingly soluble in organic solvents. (It is insoluble in acetone, chloroform or carbon tetrachloride; its solubility in methanol is low).

5.429 mg substance: 0.382 ml N_2 (20.5°, 737 mm). Found %: N 7.94. $C_{17}H_{20}O_4N_2 \cdot HCl$. Calculated %: 7.94.

Monoalkylaminoethyl Esters of β-(Naphthyl-)-acrylic Acid[2]

Butylaminoethyl ester of β-(naphthyl-1)-acrylic acid (hydrochloride). 4.5 grams of β-(naphthyl-1)-acrylyl chloride was refluxed with 2.4 g of butylaminoethanol, dissolved in chloroform saturated with hydrogen chloride, for 24 hours at 55-60°. Driving off the chloroform left behind a thick brown oil, which yielded 5.5 g of a colorless powder when it was washed with absolute ether. The initial crystallization from acetone yielded 5 g of a substance with a m.p. of 138-140°. Repeated recrystallizations from acetone and from absolute benzene yielded a substance with a m.p. of 139.5-140.5°.

The butylaminoethyl ester of β-(naphthyl-1)-acrylic acid is freely soluble in methanol, ethyl alcohol, and chloroform, and when heated in absolute ethyl alcohol, benzene, and acetone.

[1] The 5-nitro-1-naphthoic acid was produced by nitrating α-naphthoic acid with nitric acid (sp. gr. 1.4) [6].

[2] The β-(naphthyl-1)-acrylic acid was prepared by condensing α-naphthaldehyde with ethyl acetate in the presence of sodium, followed by saponifying its ethyl ester [7].

7.145 mg substance: 0.265 ml N_2 (18.5°, 748 mm). Found %: N 4.28. $C_{19}H_{23}O_2N \cdot HCl$. Calculated %: N 4.20.

Isobutylaminoethyl ester of β-(naphthyl-1)-acrylic acid (hydrochloride). 0.7 g of β-(naphthyl-1)-acrylyl chloride was heated to 60° for 24 hours with 0.4 g of isobutylaminoethanol dissolved in chloroform that was saturated with hydrogen chloride, yielding 1.1 g of a substance with a m.p. of 170-179° after the solvent had been driven off in vacuo and the residue had been washed with absolute ether. Double recrystallization from 96% ethanol yielded a substance with a m.p. of 182-183°.

6.518 mg substance: 0.254 ml N_2 (18.5°, 724 mm). 8.090 mg substance: 0.312 ml N_2 (19.5°, 741.5 mm). Found %: N 4.35, 4.38. $C_{19}H_{23}O_2N \cdot HCl$. Calculated %: N 4.20.

SUMMARY

The monoalkylaminoethyl esters of 4(5)-nitro- and 4(5)-amino-1-naphthoic acids and of β-(naphthyl-1)-acrylic acid have been synthesized.

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RESEARCH ON HYDROXYDIHYDROFURANS

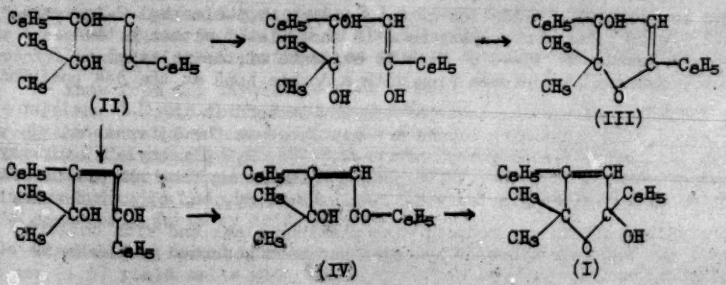
I. OXIDATION AND REDUCTION OF 2,4-DIPHENYL-5,5-DIMETHYL-2-HYDROXYDIHYDROFURAN-2,5

E. D. Venus-Danilova and A. N. Orlova

The first representative of the hydroxydihydrofurans--2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 (I)--was first synthesized by A. E. Favorsky and E. D. Venus [1] in 1915 by reacting 30% sulfuric acid (by weight) upon an acetylenic pinacol: dimethyl phenyl phenylacetenyl ethylene glycol (1,3-diphenyl-4-methylpentyne-1-diol-3,4) (II).

It was later discovered that other ditertiary alpha glycols with substituted acetylenic radicals (replaced by phenyl or tert-butyl) may also be isomerized, with varying ease, into substituted hydroxydihydrofurans [2,3,4].

The structure of the first hydroxydihydrofuran was not demonstrated experimentally. It was assigned the structure of an alcohol ether--2,4-diphenyl-5,5-dimethyl-4-hydroxydihydrofuran-4,5 (III)--and it was conjectured that this substance is formed in the partial hydration of the triple bond in the initial pinacol and the closure of the dihydrofuran ring, a molecule of water being liberated at the expense of the two hydroxyl groups in the gamma position:



A more thorough study of the nature of hydroxydihydrofuran indicated [5] that it interacts with reagents at its carbonyl group, but only when a few drops of strong acetic acid are present. Moreover, it yielded crystalline ethers of the ketal type with methanol and ethyl alcohol, and the reaction products of hydroxydihydrofuran with bromine have been investigated [5].

These findings have led us to advance another schema for the transformation of dimethyl phenyl phenylacetenyl ethylene glycol, involving an acetylenic-allenic rearrangement of the glycol, resulting in an ethylenic gamma ketol (IV), which is cyclized to the hydroxydihydrofuran-2,5 (I), instead of the hydration of the pinacol's triple bond previously proposed [1].

Subsequently, this isomerization mechanism was corroborated by the isolation of the respective ethylenic gamma ketols when certain acetylenic pinacols were isomerized [2,4,6] and by research on the bromination products of 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 [5].

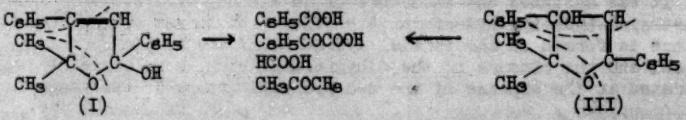
Basic properties, i.e., the ability to form salts with acids, are exhibited in greater or lesser degree by all the hydroxydihydrofurans synthesized up to the present time [1-4]. The first hydroxydihydrofuran (I) exhibits the most pronounced ability to form oxonium compounds [1]. A number of stable salts

of this substance with mineral and organic acids have been synthesized and analyzed, as well as stable complex salts with platinic, auric, and stannic chloride and with stannic bromide.

We oxidized and reduced 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5, as the most typical example of this class of compounds, in order to make a more thorough study of the properties of hydroxydihydrofurans and to resolve the problem of the variation of their basic properties with the nature and mutual position of the substituents in the hydroxydihydrofuran ring and with the structure of the five-membered ring.

Oxidation with an aqueous solution of potassium permanganate yielded acetone, benzoic acid, benzoylformic acid, and traces of formic acid.

The substances recovered do not contradict the proposed structure of the hydroxydihydrofuran [5] (I), though oxidation of the alcohol ether (III) (the structure originally advanced for hydroxydihydrofuran [1]) ought to yield analogous products. For that reason, oxidation cannot be employed to demonstrate the structure of the substance produced by isomerizing dimethyl phenyl phenylacetenyl ethylene glycol:



(I) (III)

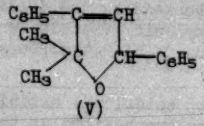
It should be noted that oxidation of 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 with potassium permanganate is incomplete, although the reaction involved heating to 35-40°. This is evidence of the relative stability of the hydroxydihydrofuran ring with a double bond at the 3-4 position.

Similar instances of the inertness of the double bond in the 3-4 position of a five-membered ring containing oxygen are mentioned in the literature, viz., 2,2-dimethyl-5,5-diphenyl-3-ethoxydihydrofuran-2,5 [7], 2,2-dimethyl-5,5-diphenyl-3-phenoxydihydrofuran-2,5 [8], the cyclic products resulting from the bromination and chlorination of 2,7-dimethyloctadiyne-3,5-diol-2,5 [9], and other substances.

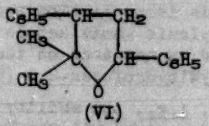
The hydroxydihydrofuran was reduced with platinum black and with colloidal palladium until two and four atoms of hydrogen had been absorbed per molecule of the hydroxydihydrofuran.

When platinum black was used, we noticed that the rate of hydrogenation dropped sharply after two hydrogen atoms had been added. Reduction was much slower when palladium was employed, though there was no perceptible change in the rate of hydrogenation.

Two products were secured when reduction was effected with two and four atoms of hydrogen. At first there settled out a crystalline substance with a m.p. of 135-137°, to which the structure of 2,4-diphenyl-5,5-dimethyldihydrofuran-2,5 (V) should be assigned on the basis of its analysis. As reduction continued, the crystals vanished, yielding a liquid with a b.p. of 158-160° at 4 mm, representing 2,4-diphenyl-5,5-dimethyltetrahydrofuran (VI).



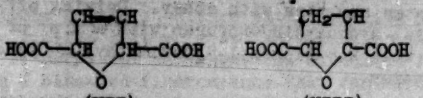
(V)



(VI)

Thus when 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran is reduced catalytically, first the hydroxyl group is reduced, and then the double bond is hydrogenated.

The production of a substituted dihydrofuran as the initial hydrogenation product is another indication of the relative strength of the double bond at the 3-4 position in an oxygen-containing five-membered ring. Similar stability of the double bond at the 3-4 position is also found in the cis and trans forms of 2,5-dihydrofuran-2,5-dicarboxylic acids (VII), which are not reduced by sodium amalgam, in contrast to the isomeric 2,3-dihydrofuran-2,5-dicarboxylic acid (VIII) [10], as well as in the properties of the bromination products of 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 [5].



(VII) (VIII) (IX)

Neither of the reduction products of the hydroxydihydrofuran is able to form oxonium compounds; the dihydrofuran does not dissolve in strong sulfuric acid, while the tetrahydrofuran produces a deep blue coloring with red fluorescence when treated with concentrated sulfuric acid, but the coloring vanishes when the mixture is diluted with water, no color being produced with strong hydrochloric acid.

Our tests lead us to conclude that the pronounced ability of 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 to form oxonium compounds is governed by the presence of the double bond in the 3-4 position of the molecule and of the hydroxyl group at the 2 position, as well as by the furan ring structure.

We know from the literature that neither 2,2,5,5-tetramethyldihydrofuran-2,5 [11] nor 2,2,5,5-tetraphenyldihydrofuran-2,5[4] [12] yields oxonium compounds, nor do the tetrahydrofurans [13]. Nor does the introduction of a hydroxyl group into the tetrahydrofuran ring produce basic properties, since the substitution derivatives of 2-hydroxytetrahydrofuran, which are cyclic forms of gamma hydroxy aldehydes and hydroxy ketones, are unstable, being converted into open-chain forms by acids [14].

It should be noted that the hydroxydihydrofurans we have synthesized up to now [1,3] yield salts with two molecules of acid, of the M·2HCl type, and that when stable complex salts are formed with platinic chloride and auric chloride, only one molecule of the acid enters into the coordination compounds: $(MH)_2PtCl_6$ and $(MH)AuCl_4$ [1-4]. This is evidence that the oxidic and hydroxyl atoms of oxygen in the hydroxydihydrofuran ring are not equivalent.

In addition to the ring structure containing oxidic oxygen, a hydroxyl group at the 2 position, and a double bond between the 3 and 4 carbon atoms in the ring, the nature and the mutual arrangement of the substituents in the hetero ring also affect the ability of hydroxydihydrofurans to form oxonium compounds. This is strikingly evident when we compare the properties of 2,4,5-triphenyl-5-methyl-[4], 2-tert-butyl-4-phenyl-5,5-dimethyl-[2], 2-phenyl-4-p-tolyl-5,5-dimethyl-[3], and 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofurans-2,5 [1]. This arrangement is most favorable in the last named compound for the pronounced appearance of basic properties (IX, R_1 and R_2 = aryl, R_3 and R_4 = alkyl) and, hence, for its ability to form oxonium salts.

EXPERIMENTAL

I. Oxidation of 2,4-Diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5

[4] This substance was placed at our disposal by S. A. Zonis, to whom we are deeply indebted.

Oxidation was effected with potassium permanganate, using 8 moles of potassium permanganate per 3 moles of the hydroxydihydrofuran. 3.2 grams of the oxidant was employed (3.17 g being called for theoretically) for 2 g of the substance. 100 ml of a 2% solution of potassium permanganate was preheated to 35-40° and then gradually added, with vigorous stirring, to the finely powdered hydroxydihydrofuran with a m.p. of 101-102°. The remaining 1.2 grams of the oxidant was added in three batches as the solution was decolorized. Oxidation was smooth under these conditions, being complete within 1.5 hours.

When oxidation was finished, the manganese dioxide was filtered out and washed with a small amount of hot water and then with ether. Driving off the ether yielded about 1 g of the initial hydroxydihydrofuran with a m.p. of 100-101°, whose mixed melting point with 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 exhibited no depression.

The steam-volatile neutral oxidation products were driven off from the filtrate into a solution of p-nitrophenylhydrazine. The yellow precipitate fused at 148°; it was the p-nitrophenylhydrazone of acetone and exhibited no depression of the melting point when mixed with the known preparation. No neutral oxidation products that were not volatile with steam were found.

The solution of salts of organic acids was concentrated on a water bath and then decomposed with dilute sulfuric acid in order to recover the acid products of oxidation. The m.p. of the precipitated light white substance, 119-120°, was that of benzoic acid; its mixed melting point with known benzoic acid exhibited no depression.

After the benzoic acid had been precipitated, the steam-volatile acids were driven off from the filtrate. All we found were slight traces of formic acid, as indicated by reactions with mercuric chloride and ammoniacal silver nitrate.

The acids that were not steam-volatile were extracted with ether; driving off the latter yielded benzoylformic acid with a m.p. of 64° [15], which threw down a flocculent precipitate with a m.p. of 153° [15] when treated with an aqueous solution of phenylhydrazine hydrochloride.

The oxidation products--acetone, benzoic acid, benzoylformic acid, and traces of formic acid--thus confirm the proposed structure of the hydroxydihydrofuran as that of 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 [5].

II. Reduction of 2,4-Diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5

1) Hydrogenation with platinum until two atoms of hydrogen had been absorbed. We used 1 g of the hydroxydihydrofuran with a m.p. of 101-102°, 80 ml of ethyl alcohol, and 0.4 g of platinum black prepared by Loew's method [16].

Hydrogenation was stopped after the 92 ml of hydrogen (19°, 160 mm) called for theoretically had been absorbed. During the course of reduction, crystals had formed; they were filtered out after reduction was over and had a m.p. of 135-137°. Driving off the alcohol yielded a light-greenish-yellow liquid, which boiled at 158-160° at the reduced pressure of 4 mm, the residue consisting of a substantial quantity of tar.

The hydrogenation test was performed three times. 3 grams of the hydroxydihydrofuran yielded 0.4 g of crystals and 1.6 g of liquid.

Analysis of the substance with a m.p. of 135-137°. The substance was sparingly soluble in alcohol, but rather freely soluble in ether and benzene. Its mixed melting point with the initial hydroxydihydrofuran exhibited

depression; it contained no hydroxyl group, did not decolorize an aqueous solution of potassium permanganate or a chloroform solution of bromine either in the cold or when heated gently, did not indicate the presence of a carbonyl group, did not dissolve in concentrated sulfuric or hydrochloric acid, and did not exhibit any fluorescence.

0.1318 g substance: 0.4180 g CO_2; 0.0838 g H_2O. Found %: C 86.49; H 7.11. $C_{18}H_{18}O$. Calculated %: C 86.40; H 7.20. 0.1398 g substance; 11.82 g C_6H_6: Δt 0.21°. Found M 282. $C_{18}H_{18}O$. Calculated M 250.

The analysis findings and the properties of the substance with a m.p. of 135-137° indicate that it is 2,4-diphenyl-5,5-dimethyldihydrofuran-2,5.

Analysis of the substance with a boiling point of 158-160° at 4 mm. The substance yielded neither a semicarbazone nor an oxime, decolorized an aqueous solution of potassium permanganate, dissolved in concentrated sulfuric acid, producing a blue-red fluorescence that vanished upon dilution with water, and dissolved sparingly in strong hydrochloric acid, exhibiting no perceptible fluorescence.

0.1215 g substance: 0.3796 g CO_2; 0.0872 g H_2O. 0.0943 g substance: 0.2972 g CO_2; 0.0694 g H_2O. Found %: 85.21, 85.95; H 7.97, 8.17. $C_{18}H_{20}O$. Calculated %: C 85.71; H 7.93. 0.1742 g substance; 11.29 g C_6H_6: Δt 0.30°. Found M 253. $C_{18}H_{20}O$. Calculated M 252.

The substance with a b.p. of 158-160° at 4 mm must be 2,4-diphenyl-5,5-dimethyltetrahydrofuran.

2) Hydrogenation with platinum until four hydrogen atoms had been added. The quantities of the substance, the alcohol, and the catalyst used were the same as in the preceding test, but hydrogenation was stopped after four atoms of hydrogen had been added (the theory called for 182 ml at 17° and 766 mm).

We noted that the rate of hydrogenation dropped sharply after two atoms of hydrogen had been added (the rate dropping to about one-tenth of its former value). Here, again, crystals with a m.p. of 135-137° settled out at first, their quantity diminishing as reduction continued, the bulk of the end product consisting of a liquid with a b.p. of 158-160° at 4 mm.

Both the crystals and the liquid were identical with the hydrogenation products secured in the first test. This was evidenced by the properties of the substances as well as by their elementary analysis.

We ran five hydrogenation tests in all, 5 g of the hydroxydihydrofuran yielding 0.3 g of crystals and 3 g of the liquid product.

3) Hydrogenation with colloidal palladium. 1.5 grams of colloidal palladium [17] was added to a solution of 0.3 g of the hydroxydihydrofuran in 60 ml of ethyl alcohol. It was found that here, again, a crystalline substance with a m.p. of 135-137° settled out after 27.2 ml of hydrogen (16°, 755 mm) had been added, equivalent to two atoms of hydrogen per mole of the hydroxydihydrofuran. After the crystals had been filtered out, 1 ml of colloidal palladium was added to the solution, and reduction was continued until another two atoms of hydrogen had been absorbed per mole of the hydroxydihydrofuran. This yielded a liquid, which could only be analyzed qualitatively, owing to the minute quantity recovered. Its properties were those of the liquid recovered when the hydroxydihydrofuran was reduced with platinum black.

SUMMARY

1. When 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran-2,5 is reduced with platinum black or with colloidal palladium, first the hydroxyl group is reduced and then the double bond.

2. Two reduction products were isolated: a crystalline substance with a m.p. of 135-137°, representing 2,4-diphenyl-5,5-dimethyldihydrofuran-2,5, and a liquid substance with a b.p. of 158-160° at 4 mm, which must be assigned the structure of 2,4-diphenyl-5,5-dimethyltetrahydrofuran.

3. The structure of 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran is confirmed by its oxidation products: acetone, benzoic acid, benzoylformic acid, and traces of formic acid.

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THE CATALYTIC DEHYDRATION OF 2,2,5,5-TETRAALKYL- AND 2,5-DIALKYLFURANIDINES IN AN ATMOSPHERE OF HYDROGEN SULFIDE

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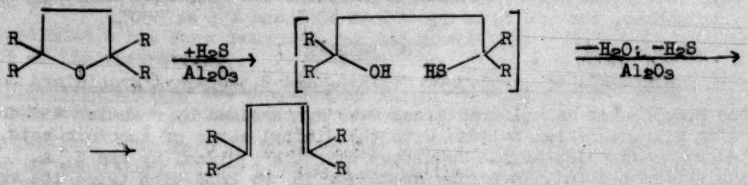
The present paper discusses the behavior of 2,2,5,5-tetramethyl-, 2,2,5,5-tetraethyl-, and 2,5-diethylfuranidines when reacted with hydrogen sulfide at high temperature in the presence of alumina.

It has been found that, in contrast to furanidine and others of its homologs [1], the tetraalkylfuranidines are not transformed into the respective thiophanes, but rather into diene hydrocarbons with conjugated double bonds: 2,5-dimethylhexadiene-2,4 (30% of the theoretical yield) from 2,2,5,5-tetramethylfuranidine and 3,6-diethyloctadiene-3,5 (27.5% of the theoretical) from 2,2,5,5-tetraethylfuranidine.

The catalytic dehydration of furanidine and of its homologs has been described in the literature [2], a 45% yield of a mixture of diene hydrocarbons, consisting of 16% of hexadiene-1,3, 45% of hexadiene-1,4, and 35% of hexadiene-2,4, having been secured by passing 2-ethylfuranidine in a current of nitrogen over aluminum phosphate at 400°. It was extremely difficult to dehydrate 2-methylfuranidine under these conditions, only 25% of the oxide undergoing conversion, while the composition of the resultant complex mixture of hydrocarbons was not established [3].

The fact that 2,2,5,5-tetraalkyl furanidines cannot be converted into the respective thiophanes is doubtless due to the ditertiary mercaptohydroxy compounds that are formed as intermediate products under the action of hydrogen sulfide (which vigorously attacks the carbon-oxygen bond of the oxide) splitting off water as well as hydrogen sulfide readily, resulting in the formation of a conjugated diene hydrocarbon:

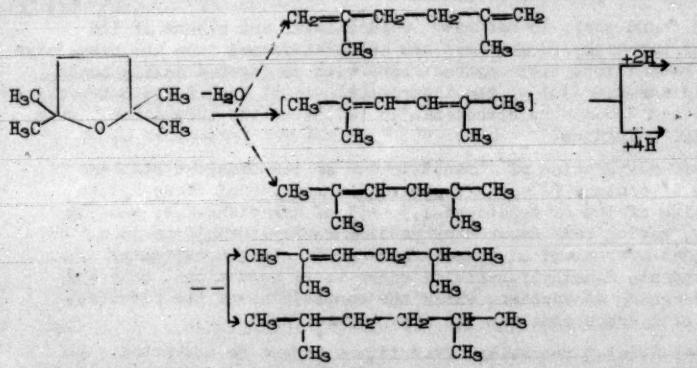


It should be stressed that the smooth formation of conjugated dienes and the preservation of these dienes unchanged were aided in the present instance by our having dehydrated the 2,2,5,5-tetraalkylfuranidines catalytically in an atmosphere of hydrogen sulfide. When 2,2,5,5-tetramethylfuranidine was dehydrated in this manner at 350°, the reaction product consisted of practically nothing but 2,5-dimethylhexadiene-2,4 (diisocrotyl).

When no hydrogen sulfide was present--the 2,2,5,5-tetramethylfuranidine being dehydrated over alumina at 350° in a current of nitrogen, we secured a mixture of unsaturated hydrocarbons, which could not be sharply separated by distillation into a column with an efficiency of 25 theoretical plates, the bulk of the distillate passing over below the boiling point of diisocrotyl, but again containing as much as 25% (by weight of the resulting condensate) of high-boiling polymeric forms. Investigation of the Raman spectra of the fractions secured from the catalyzate demonstrated that the tested hydrocarbon mixture

contained, besides the 2,5-dimethylhexadiene-2,4, other unsaturated hydrocarbons: 2,5-dimethylhexadiene-1,5 (diisobutyl); cis-2,5-dimethylhexene-2; trans-2,5-dimethylhexene-2; and, possibly, 2,5-dimethylhexane.

The 2,5-dimethylhexene-2 was evidently produced as the result of partial hydrogenation of the 2,5-dimethylhexadiene-2,4 (at the 1,2 positions, i.e., in conformity with the rule established by R. Ya. Levina and V. R. Skvarchenko [4] in the partial hydrogenation of 2,5-dimethylhexadiene-2,4 by sodium-ammonium) by the hydrogen evolved in the decomposition of part of the molecule; the 2,5-dimethylhexane was formed by the complete hydrogenation of the 2,5-dimethylhexadiene-2,4:



As for the 2,5-diethylfuranidine, it was converted into 2,5-diethylthiophane when acted upon by hydrogen sulfide at 350° in the presence of alumina, though the yield was low (12% of the theoretical) and the reaction entailed the formation of a mixture of unsaturated hydrocarbons. Under these same conditions the 2,5-dimethylfuranidine was converted into 2,5-dimethylthiophane, the yields being 68% at 400° and 43% at 350°.

EXPERIMENTAL

Synthesis of 2,2,5,5-Tetraalkyl- and 2,5-Dialkylfuranidines

The 2,2,5,5-tetraalkylfuranidines were synthesized by reacting the corresponding alkylmagnesium halides with the diethyl ester of succinic acid, followed by dehydration of the resultant ditertiary glycol by the Z. A. Pogorzhelsky method [6], involving agitation in the cold with twice its volume of 66% sulfuric acid.

1) 2,2,5,5-Tetramethylfuranidine had the following constants after distillation into a column with an efficiency of 25 theoretical plates:

B.p. 112° (756 mm); n_D^{20} 1.4050; d_4^{20} 0.8013; MR_D 38.32; Calculated 38.59.

Figures in the literature for 2,2,5,5-tetramethylfuranidine: b.p. 113° (786 mm); d_4^{20} 0.8113 [5]; b.p. 116-117° [6]; b.p. 117.5° [7].

2) 2,2,5,5-Tetraethylfuranidine:

B.p. 75-76° (7 mm); n_D^{20} 1.4440; d_4^{20} 0.8612. MR_D 56.76; Calculated 57.06.

Figures in the literature for 2,2,5,5-tetraethylfuranidine: Yu. S. Zalkind [8]: b.p. 89-90° (8 mm), 204-206°, 95-96 (14 mm) [9].

3) 2,5-Diethylfuranidine was prepared by reacting an Iotsich coordination compound [10] with propionaldehyde, followed by hydrogenating the resultant octyne-4-diol-3,6 to octanediol-3,6 and dehydrating the latter by the Pogorzhelsky method.

Octyne-4-diol-3,6. 43.5 grams of propionaldehyde in an equal volume of ether was chilled and then added to an Iotsich coordination compound, prepared from 18 g of magnesium, 90 g of ethyl bromide, and 200 ml of ether. Then the reaction mixture was heated for an hour and a half on a water bath, and the next day it was decomposed by water and 50% acetic acid. The combined ether extracts were dried and the ether driven off, after which the octyne-4-diol-3,6 was distilled in a current of nitrogen.[1])

B.p. 119° (4 mm); n_D^{20} 1.4703; d_4^{20} 0.9786. MR_D 40.56; Calculated 40.19; ΣM_D +0.37.

The exaltation of the molecular refraction corresponds to the exaltation values found by V. N. Krestinsky and N. Persiantseva [11] for acetylenic glycols; ca. +0.4 to +0.5.

8.540 mg substance: 21.140 mg CO_2; 7.620 mg H_2O. 4.580 mg substance: 11.340 mg CO_2; 4.085 mg H_2O. Found %: C 67.51, 67.53; H 9.99, 9.98 $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.93.

Octane-diol-3,6 was prepared by hydrogenating octyne-4-diol-3,6 (using 10 g of the diol in 50 ml of absolute alcohol and 0.45 g of platinum black). Hydrogenation was stopped after 90% of the calculated amount of hydrogen had been absorbed. Distillation yielded the octanediol-3,6 as a faintly yellowish, viscous liquid with the following constants:

B.p. 102.5-104° (1 mm); n_D^{20} 1.4532; d_4^{20} 0.9331. MR_D 41.79; Calc. 42.35 ΣM_D −0.6.

The depression of the molecular exaltation of octanediol-3,6 agreed with the values of this depression (ca. -0.7 to -0.9) found by V. N. Krestinsky and N. Periantseva for saturated glycols [11].

5.005 mg substance: 12.050 mg CO_2; 5.610 mg H_2O. 5.830 mg substance: 14.050 mg CO_2; 6.500 mg H_2O. Found %: C 65.66, 65.73; H 12.54, 12.45. $C_8H_{18}O_2$. Calculated %: C 65.71; H 12.41.

Octanediol-3,6 has been described for the first time. The yield totaled 7.1 g (70% of the theoretical).

2,5-Diethylfuranidine was prepared by the Z. A. Pogorzhelsky method [5], 9.5 g of octanediol-3,6 yielding 5 g of the oxide (59% of the theoretical yield).

B.p. 142-143° (760 mm); n_D^{20} 1.4215; d_4^{20} 0.8419. MR_D 38.59; Calc. 38.47.

6.240 mg substance: 17.150 mg CO_2; 7.010 mg H_2O. 4.350 mg substance: 11.490 mg CO_2; 4.860 mg H_2O. Found %: C 74.96, 74.86; H 12.57, 12.50. $C_8H_{16}O$. Calculated %: C 74.94; H 12.55.

2,5-Diethylfuranidine has been described for the first time.

Catalytic Dehydration of 2,2,5,5-Tetraalkylfuranidines in Hydrogen Sulfide

1) 2,2,5,5-Tetramethylfuranidine was passed over alumina in a current of hydrogen sulfide at a rate of 8-10 drops per minute at 250, 320, and 400°. The catalyzate was saturated with alkali, washed with water, and extracted with ether. The ether extracts were dried with potassium hydroxide, the ether was driven off, and the residue was distilled into a column with an efficiency of 25 theoretical plates.

[1]) Octyne-4-diol-3,6 has been described for the first time. The yield totaled 26.5 g (50% of the theoretical).

250°. Distillation of the catalyzate secured from 18 g of 2,2,5,5-tetramethylfuranidine yielded the following fractions: I up to 113°--0.9 g; II 113-133.5°--a few drops; III 133.5-134.5° (762 mm)--4 g; and IV 134.5-148°--0.7 g. The fractions contained no sulfur compounds.

Fraction III, with a b.p. of 133.5-134.5°, decolorized bromine water and a permanganate solution, crystallized upon cooling, and constituted 2,5-dimethylhexadiene-2,4 (diisocrotyl), the yield being 26% of the theoretical).

n_D^{20} 1.4753; d_4^{20} 0.7697. MR_D 40.36; Calc. 38.21; ΣM_D +2.16.

320°. Distillation of the catalyzate secured from 15 g of 2,2,5,5-tetramethylfuranidine yielded the following fractions: I up to 113°--0.6 g; II 113-133.5°--a few drops; III 133.5-134°--0.3 g; IV 134-134.4° (760 mm)--4.3 g; and V 134.4-145°--0.6 g. The fractions contained no sulfur compounds.

Fraction IV was 2,5-dimethylhexadiene-2,4, the yield being 30% of the theoretical.

B.p. 134-134.4° (760 mm); n_D^{20} 1.4772; d_4^{20} 0.7665. MR_D 40.63; Calc. 38.21; ΣM_D+2.42.

3.970 mg substance: 12.670 mg CO_2; 4.515 mg H_2O. 5.179 mg substance: 16.520 mg CO_2; 5.967 mg H_2O. Found %: C 87.09, 87.05; H 12.72, 12.89. C_8H_{14}. Calculated %: C 87.19; H 12.81.

Figures in the literature for 2,5-dimethylfuranidine-2,4: A. E. Favorsky [12]: b.p. 134-135° (768.8 mm); Z. A. Pogorzhelsky [5]: b.p. 132-134°; S. V. Lebedev [13]: b.p. 75° (100 mm); Prevost [14]: b.p. 134.6° (750 mm); $n_D^{19.5}$ 1.4796; d_4^{20} 0.7646. R. Ya. Levina and assoc. [15]: b.p. 134-134.5°, (747 mm); n_D^{20} 1.4760; d_4^{20} 0.7636.

400°. Distillation of the catalyzate secured from 12 g of 2,2,5,5-tetramethylfuranidine yielded the following fractions: I 102-116°--2.8 g; 116-130°--0.8 g; III 130-133.8°--0.2 g; IV 133.8-134.5°--2.6 g; and V 134.5-150°--1.35 g. The fractions contained no sulfur compounds.

Fraction IV was 2,5-dimethylhexadiene-2,4, the yield being 25% of the theoretical.

B.p. 133.8-134.5° (760 mm); n_D^{20} 1.4769; d_4^{20} 0.7698. MR_D 40.61; Calc. 38.21; ΣM_D+2.40.

2) 2,2,5,5-Tetraethylfuranidine was passed over alumina in a current of hydrogen sulfide at 275 and 325°.

325°. The catalyzate (10.4 g) secured from 20 g of the oxide was distilled into a column with an efficiency of 25 theoretical plates, yielding 4.2 g of a hydrocarbon with a b.p. of 197-199° (750 mm); n_D^{20} 1.4615 and d_4^{20} 0.8085.

275°. Distillation of the catalyzate (11.3 g) secured from 20 g of the oxide yielded 5 g of a hydrocarbon (27.5% of the theoretical yield) with a b.p. of 200-201.5° (762 mm); n_D^{20} 1.4621 and d_4^{20} 0.8092.

The synthesized preparations decolorized bromine water and a potassium permanganate solution and contained no sulfur. Redistillation (into the column) of the combined preparations yielded a hydrocarbon possessing the following constants:

B.p. 199.5-200.5° (751 mm); n_D^{20} 1.4600; d_4^{20} 0.8098. MR_D 56.24; Calc. 56.68.

This hydrocarbon must be 3,6-diethyloctadiene-3,5 (not described in the literature), but the absence of exaltation of the molecular refraction and the analysis results indicate that it contained a slight trace of the initial oxide that could not be eliminated by distillation.

4.645 mg substance: 14.305 mg CO_2; 5.500 mg H_2O. 5.620 mg substance: 17.325 mg CO_2; 6.695 mg H_2O. Found %: C 84.02, 84.10; H 13.25, 13.32. $C_{12}H_{22}$. Calculated %: C 86.66; H 13.35. $C_{12}H_{24}O$. Calculated %: C 78.19; H 13.13.

Hence, passing 2,2,5,5-tetraethylfuranidine over alumina in a strong current of hydrogen sulfide yielded as one of the reaction products the diene hydrocarbon $C_{12}H_{22}$, no sulfur-containing compound being produced. The synthesized hydrocarbon polymerized upon standing.

Conversion of 2,5-Diethylfuranidine Into 2,5-Diethylthiophane

9 grams of 2,5-diethylfuranidine was passed over alumina at 350° at the rate of 8 drops per minute in a current of hydrogen sulfide. The ether extracts of the catalyzate were dried with potassium hydroxide, the ether driven off, and the residue distilled from a flask fitted with a dephlegmator.

Distillation yielded two fractions: I b.p. 76-150°; and II b.p. 150-200°. Double distillation of Fraction II yielded 1.2 g of 2,5-diethylthiophane (12% of the theoretical yield), possessing the following constants:

B.p. 183.5-184.5° (1760 mm); n_D^{20} 1.4825; d_4^{20} 0.9104. MR_D 45.16; Calc. 44.72. 5.436 mg substance: 8.730 mg $BaSO_4$. Found %: S 22.05. $C_8H_{16}S$. Calculated %: S 22.22.

Subsequent redistillations of the fraction with a b.p. of 76-150° yielded a hydrocarbon fraction with a b.p. of 125-127° (1.1 g), which decolorized bromine water and a potassium permanganate solution and contained no sulfur. This fraction was not investigated further.

Under the same conditions (350°) 2,5-dimethylfuranidine (9 g) yielded 4.5 g of 2,5-dimethylthiophane (43% of the theoretical yield).

B.p. 140-141° (760 mm); n_D^{20} 1.4818; d_4^{20} 0.9235. MR_D 35.85; Calc. 35.68. Figures in the literature for 2,5-dimethylthiophane: Yu. K. Yurev [1]: b.p. 140.2--140.8° (758 mm); n_D^{20} 1.4822; d_4^{20} 0.9220.

Catalytic Dehydration of 2,2,5,5-Tetramethylfuranidine With No Hydrogen Sulfide Present

50 grams of 2,2,5,5-tetramethylfuranidine were passed over alumina at 350° in a gentle current of nitrogen. The hydrocarbon layer of the catalyzate (27 g) was desiccated with potassium chloride and then distilled into a column with an efficiency of 25 theoretical plates (see table).

Fraction No.	Grams	Boiling point at 760 mm	n_D^{20}	d_4^{20}
I	1.4	45--100°	—	—
II	1.8	100--107	1.4178	0.7372
III	2.2	107--111.4	1.4180	0.7372
IV	3.6	111.4--115.5	1.4204	0.7385
V	5.2	115.5--129	1.4412	0.7709
VI	1.4	129--150	1.4644	0.7832
VII	5.9	150--245	(Distilled from a flask fitted with a small dephlegmator)	
Residue		Tar		

All the fractions decolorized bromine water and a solution of potassium permanganate.

Redistillation of Fractions V and VI yielded 1.7 g of a fraction with a b.p. of 115.5-120°; n_D^{20} 1.4358; 1.5 g of a fraction with a b.p. of 120-124°; n_D^{20} 1.4390; and 1.8 g of a fraction with a b.p. of 124-129.5°; n_D^{20} 1.4480.

The fractionation data indicated that the product of the dehydration of 2,2,5,5-tetramethylfuranidine in a current of nitrogen was a mixture of unsaturated hydrocarbons, from which 2,5-dimethylhexadiene-2,4 could not be isolated in the pure state.

Several of these fractions were combined together (in view of the closeness of their constants) in order to investigate the composition of this mixture by means of Raman spectra.

The Raman spectra were recorded with a three-prism glass spectrograph with a mean dispersion of 13 A/mm in the 4358-4916 A region, using a slit width of 0.1 mm, equivalent to approx. 6 cm^{-1} in the spectrum. The excitation for the spectrum was furnished by the Hg line of 4358 A (using a KNO_2 light filter).

The apparatus and the procedure employed have been described in detail earlier [16].

The spectra of the pure 2,2,5,5-tetramethylfuranidine and of four fractions of the catalyzate secured when the 2,2,5,5-tetramethylfuranidine was dehydrated over alumina are given below.

In the spectra the relative blackening is indicated in parentheses after the frequencies, the blackening being measured in the microphotograms, with the exception of the fraction with a b.p. of 115.5-124°, in whose spectrum the blackening of the strongest lines was estimated visually owing to the intensity of the background.

The quantitative composition of the fractions was estimated from the intensity (on an objective scale) of the lines for the pure substances that might be present in the fractions analyzed and by the blackening of the corresponding lines in the spectra; it is approximative.

In the fraction with a b.p. of 100-111.4° the frequencies of 315, 442, 470, 505, 541, 593, 769, 850, 917, 930, 956, 1071, 1104, 1177, 1335, 1382, and 1672 cm^{-1} indicate the presence of some 25% of trans-2,5-dimethylhexene-2 [4]. The trans-2,5-dimethylhexene-3 is apparently not present, since the spectrum does not exhibit the strongest line of this hydrocarbon, 460 cm^{-1} [4]. We attribute the 1657 cm^{-1} line to cis-2,5-dimethylhexene-2, the percentage of which we estimate to be about 25%. The rest of this fraction apparently consists of alkanes (possibly 2,5-dimethylhexane), the presence of which is evinced by the extremely strong band 1439-1456 cm^{-1} (deformation oscillation of the CH_2 group). The fraction tested can have only traces of the initial 2,2,5,5-tetramethylfuranidine, inasmuch as the spectrum does not display the strongest lines in this oxide's spectrum, 583 and 908 cm^{-1}.

The frequencies found in the fraction with a b.p. of 111.4-115.5°: 257, 327. 380b, 390, 416b, 434, 494, 530, 760, 854, 890, and others, as well as 1649 and 1672 cm^{-1} indicate the presence of the following: some 15% of 2,5-dimethylhexadiene-1,5 (diisobutenyl) [17]; and 2,5-dimethylhexene-2, its trans form totalling some 45-50% and its cis form some 30% (on the assumption that the intensities of the characteristic bands--1658 cm^{-1} for the cis form and 1672 cm^{-1} for the trans form--are about 120 units on the so-called cyclohexane scale, on which I_{801} of cyclohexane equals 250 per mole and cm^{-1}). An alkane may be present (though not exceeding 10%). There is practically no 2,5-dimethylhexadiene-2,4 (diisocrotyl) in this fraction, since the fraction's spectrum does not exhibit the very strong lines of this hydrocarbon: 1156 (750), 1226 (320), and 1366 (340) cm^{-1} (the intensities within parentheses are given in units of the cyclohexane scale).

The fractions with b.p. of 115.5-124° and 124-129.5° could not be deciphered in their entirety, though the presence of the following frequencies [4]: 295,343,468, 839, 862, 1023-1040d, 1065, 1096, 1155, 1225, 1330d, 1364, 1382, 1443-1456, 1648, and 1665 cm^{-1} indicates that they contain substantial amounts of 2,5-dimethylhexadiene-2,4, no less than 70% in the fraction with a b.p. of 124-129.5°.[1])

Spectrum of 2,2,5,5-tetramethylfuranidine. $\Delta\nu$=248(3) r,d; 282 (2); 310 (12); 352(5); 370(7); 421(4)d; 452(3); 583(38); 740(7); 768(51); 850(9); 908(22); 942(9); 964(7); 1000(11); 1025(3); 1079(12); 1133(5); 1215(16); 1245(11); 1268(11); 1315(3)d; 1445(24); 1464(24).

Spectra of the Products of the Dehydration of 2,2,5,5-Tetramethylfuranidine

1. Fraction with a b.p. of 100-111.4°. $\Delta\nu$ = 265(4)d; 315(4)r; 335(7); 390(3)d; 413(4)d; 442(2); 470(3); 505(4); 541(8); 567(13); 593(6); 648(5); 705(4); 769(10)r; 805(7)h; 824(7)h; 850(8)d; 890(5); 917(5); 930(6); 956(8); 1001(3); 1035(8); 1071(4); 1104(11)r; 1150(5)d; 1177(5); 1204(5); 1299(6)r; 1335(7); 1382(14); 1439-56(42)r,s; 1657(24); 1672(21).

2. Fraction with a b.p. of 111.4-115.5°. $\Delta\nu$ = 257--95(3)r,d ; 322(5); 387--97(5)d ; 421--47(5)r, d; 470(6); 490(5); 530(4); 547(4); 570(3); 587(5); 773(17); 803(6); 850(11)r, s ; 890(7)r; 921(5); 940(4)d; 960(14); 1015(8); 1032(7); 1071(6); 1090(1); 1107(14)r; 1150(2); 1170(8); 1196--1204(3)d; 1246(5); 1270(6); 1301(5); 1332(16); 1382(24); 1446--64(42); 1647--61(29) s ; 1672(49).

3. Fraction with a b.p. of 115.5-124°. $\Delta\nu$ = 295r,d ; 406--21r,d ; 468; 537; 608; 628; 683(2); 764; 771; 811; 839(3); 862(3); 893; 943; 960; 1015-40r; 1074; 1098r ; 1157(5); 1170; 1212; 1225; 1270; 1299; 1317; 1332; 1367; 1382(10); 1440-56(10); 1650(8); 1665(20); 1680(8).

4. Fraction with a b.p. of 124-129.5°. $\Delta\nu$ = 295(4)r; 343(3); 414(3)d; 445(2); 468(5); 502(3); 534(4); 587(5); 631(2); 683(5)r; 728(3); 764(3)d; 811(4); 839(9); 862(9); 1000(2); 1023-40(3)d; 1065(6); 1096(8)r; 1155(28); 1225(22); 1330(6)d; 1364(5); 1382(30); 1443-56(33); 1648(25); 1665(30); 1680(10).

SUMMARY

1. When 2,2,5,5-tetramethylfuranidine comes into contact with alumina at 350° in an atmosphere of hydrogen sulfide, the only reaction taking place is dehydration, the principal reaction product being 2,5-dimethylhexadiene-2,4 (diisocrotyl), and its yield being 30% of the theoretical.

When no hydrogen sulfide is present, the contact of 2,2,5,5-tetramethylfuranidine with alumina at 350° yields a mixture of unsaturated hydrocarbons, containing 2,5-dimethylhexadiene-1,5 (diisobutenyl), 2,5-dimethylhexene-2 (the cis and trans isomers), possibly 2,5-dimethylhexane, and high-boiling polymers, in addition to the 2,5-dimethylhexadiene-2,4.

2. When 2,2,5,5-tetraethylfuranidine comes into contact with alumina in an atmosphere of hydrogen sulfide, the principal reaction product (27.5% yield) is again a diene hydrocarbon: 3,6-diethyloctadiene-3,5, that apparently contains an inseparable trace of the initial oxide.

[1]) We are indebted to V. M. Tatevsky for his counsel in the optical analysis of the chemical nature of the dehydration product of 2,2,5,5 -tetramethylfuranidine.

3. When 2,2,5,5-tetraalkylfuranidines are acted upon by hydrogen sulfide, they cannot be transformed catalytically into the corresponding thiophanes because the mercapto hydroxy compounds formed as intermediates are ditertiary and they all split out water and hydrogen sulfide with ease.

4. When 2,5-dimethyl- and 2,5 diethylfuranidine are reacted with hydrogen sulfide at 350° in the presence of Al_2O_3, they are converted into 2,5-dimethylthiophane and 2,5-diethylthiophane, respectively.

5. In conformity with the rule established by R. Ya. Levina and V. R. Skvarchenko, the 2,5-dimethylhexadiene-2,4 is partially hydrogenated by hydrogen at the instant of its formation (as took place in the catalytic dehydration of 2,2,5,5-tetramethylfuranidine at 350° with no hydrogen sulfide present) at the 1,2 position, resulting in the formation of a mixture of the cis and trans isomers of 2,5-dimethylhexene-2.

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1) See Consultants Bureau English Translation, p. 721.
2) See Consultants Bureau English Translation, p. 727.

RESEARCH ON THE ALKALOIDS OF Eremosparton flaccidum Litw

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The Central Asian subsurface plant Eremosparton flaccidum Litw, which belongs to the legume family (Leguminosae), grows in the eastern Kara-Kum. The presence of alkaloids in Eremosparton flaccidum Litw was discovered for the first time in 1932 by P. S. Massagetov, head of the expedition of the S. M. Ordzhonikidze All-Union Research Institute of Pharmaceutical Chemistry (AURIPC). Pharmacological examination of the raw material he had collected indicated that an extract of the green portions of this plant lowered blood pressure greatly without affecting respiration.

We subjected this plant to chemical examination for the first time in the spring of 1941. All endeavors to isolate individual alkaloids from the green portions of Eremosparton Flaccidum Litw in the usual manner, i.e., extraction as bases with an organic solvent, followed by treating the resulting solution with sulfuric acid, resulted in a highly tarred, strongly basic mixture of alkaloids. Further processing did not yield individual alkaloids; only distillation in vacuo at 3-4 mm yielded minute quantities of two substances that underwent change when exposed to the air and were converted into hydrochlorides by the action of alcoholic hydrochloric acid. The composition of one of them, with a m.p. of 129-130°, most closely approximated the formula $C_9H_{20}O_4N_4 \cdot 2HCl$. The formula for the second hydrochloride, with a m.p. of 262°, was $C_9H_{20}ON_2 \cdot 2HCl$. Both the formula and the melting point of this substance were those of the dihydrochloride of isopropylvinylputrescine, prepared by the hydrolytic cleavage of spherophysine, isolated by M. M. Rubinshtein and G. P. Menshikov [1] from the Central Asian plant Sphaerophysa salsula, which also belongs to the legume family.

Since the amount of the substance we had isolated proved to be insufficient for a direct comparison with the dihydrochloride of isopropylvinylputrescine, even by determining their mixed melting point, we treated the plant to secure the alkaloids, but this time by a method resembling the procedure specified by the foregoing authors for the recovery of spherophysine from Sphaerophysa salsula. The alkaloids were recovered as carbonates, hydrolytic cleavage of which yielded a diamine that was identified as the diamine isolated from spherophysine by directly comparing their picrates and hydrochlorides. Their mixed melting points exhibited no depression. We also isolated another product of the hydrolytic cleavage of spherophysine-urea, which was identified as its nitrate and succinate, and, lastly, we isolated and identified spherophysine carbonate by refining the total carbonates. The comparative data are listed in the following table:

	From Eremosparton flaccidum Litw, melting point	From Sphaerophysa salsula, melting point
Spherophysine carbonate	192-193°	192-193°
Spherophysine benzoate.....	149-150	149-150
Isopropylvinylputrescine hydrochloride	262-263	262-263
Isopropylvinylputrescine picrate	180-181	180-181

It was subsequently discovered that spherophysine is found not only in Spherophysa salsula and Eremosparton flaccidum Litw, but also in a third plant of this family. A. A. Ryabinin, for example, has isolated spherophysine from Smirnovia turkestana Bge.

EXPERIMENTAL

Extraction of Eremosparton flaccidum Litw with dichloroethane. 5 kg of the dried and finely pulverized green portions of the plant was wetted with 10% ammonia and then extracted with dichloroethane until all the alkaloids had been extracted. The dichloroethane solution was treated with 10% sulfuric acid, the acid solution being neutralized with 25% ammonia, dried with potash, and extracted first with ether and then with chloroform. Driving off the ether yielded 1.54 g (or 0.031% of the plant weight) of a light-yellow mixture of alkaloids, which were sparingly soluble in water, had almost no alkaline properties, and contained traces of essential oils. Driving off the chloroform yielded 4.65 g (0.093% of the plant weight) of a black, tarry, strongly alkaline mixture of alkaloids. The alkaloids of this fraction were freely soluble in water and absorbed carbon dioxide when allowed to stand exposed to the air.

The alkaloids of both fractions are strongly tarred by the action of acids, yield no crystalline salts, and decolorize permanganate in sulfuric-acid solution. Hydrogen is absorbed when they are hydrogenated with a Pt catalyst, but the resultant substance does not yield crystalline salts either. Separating the total alkaloids into fractions according to their basicity or according to their solubility in various solvents failed to yield the individual substances.

Distillation of the chloroform fraction in vacuo. Two fractions were collected when the mixture of alkaloids secured by extraction with chloroform was distilled at a 3-4 mm vacuum. The first fraction distilled at 98-100° and was for the most part a crystalline substance that was highly hygroscopic and volatile. It was converted into a hydrochloride by the action of alcoholic hydrochloric acid, the mother liquor quickly turning black and tarring completely after the crystalline matter had been filtered out. Recrystallization from boiling acetone yielded the hydrochloride as thin colorless needles with a m.p. of 129-130°.

3.214 mg subst.: 3.982 mg CO_2; 2.074 mg H_2O. 2.477 mg subst.: 0.355 ml N_2 (24°, 735 mm). 6.205 mg subst.: 5.762 mg AgCl. Found %: C 33.79; H 7.17; N 16; Cl 22.99. $C_9H_{20}O_4N_4 \cdot 2HCl$. Calculated %: C 33.64; H 6.85; N 17.4; Cl 22.12.

The aqueous solution of the hydrochloride had an acid reaction and yielded no precipitate at all with silicowolframic acid, in contrast to the mother liquor, which yielded an abundant precipitate.

The second fraction, distilling at 100-115°, was a liquid. Reacting it with alcoholic hydrochloric acid yielded the hydrochloride, which crystallized from alcohol as lustrous colorless lamellae with a m.p. of 262°, which produced neutral aqueous solutions. After the hydrochloride had been filtered out, the acid mother liquor blackened and tarred.

3.214 mg substance: 3.932 mg CO_2; 2.074 mg H_2O. 2.477 mg substance: 0.355 ml N_2 (24°, 735 mm). 6.205 mg substance: 5.762 mg AgCl. Found %: C 33.79; H 7.17; N 16; Cl 22.99. $C_9H_{20}O_4N_4 \cdot 2HCl$. Calculated %: C 33.64; H 6.85; N 17.4; Cl 22.12.

Extraction of Eremosparton flaccidum with alcohol from the acid solution. 1 kg of air-dry green portions of the plant was extracted three times with alcohol, slightly acidulated with acetic acid. After the alcohol had been driven off in vacuo, the residue was diluted with water, and the voluminous precipitate, which contained chloroform, was suction-filtered. The filtrate was strongly alkalinized with a 40% solution of sodium hydroxide and extracted with chloroform.

The alkaloid was extracted from the filtered chloroform solution by distilled water, the aqueous alkaline solution being saturated with carbon dioxide and all the water being driven off at 40-45° in a 20mm vacuum. The crystalline precipitate was a mixture of alkaloid carbonates and inorganic carbonates.

Hydrolytic cleavage of the carbonates. Half of the residue was subjected to hydrolytic cleavage by the Rubinshtein and Menshikov method, using barium hydroxide[1]. The liquid base produced was converted into the hydrochloride with a m.p. of 262-263° and the picrate with a m.p. of 180-181°. Neither salt exhibited a depression of the mixed melting point with the respective salt of isopropylvinylputrescine, prepared by the hydrolytic cleavage of spherophysine.

Appropriate treatment by the same method of the aqueous solution obtained after the base had been eliminated yielded urea. The characteristic urea nitrate with a m.p. of 149° and urea succinate with a m.p. of 142° were prepared.

Isolation of spherophysine carbonate. The other half of the carbonate mixture was freed of its inorganic salts by means of absolute alcohol. Triple recrystallization from absolute alcohol yielded the substance as white needles, melting with decomposition at 192-193°. Its mixed melting point with spherophysine carbonate exhibited no depression. The benzoate prepared from the carbonate had a m.p. of 149-150°. Its mixed melting point with spherophysine benzoate did not exhibit any depression either.

SUMMARY

Two substances have been isolated from the Central Asian plant Eremosparton flaccidum Litw (Leguminosae family), one of them proving to be spherophysine, which was previously isolated from Sphaerophysa salsula of the same family.

The other substance, whose hydrochloride has a formula that approximates $C_9H_{20}O_4N_4 \cdot 2HCl$, was recovered in an extremely minute amount, and has been subjected only to preliminary study as yet.

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DISCUSSION

A. M. BUTLEROV'S THEORY OF CHEMICAL STRUCTURE AND ITS RECENT SUCCESSES

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The problems of chemical structure continue to hold the center of the stage in the Soviet chemical world. The existent confusion in chemical theory is a serious obstacle to the scientific, practical, pedagogical, and ideological work of chemists. The contemporary practical and methodological problems of chemical theory can be solved only along the lines of A. M. Butlerov's theory of chemical structure, which has been tested in the widest practical applications and is therefore reliable. An attempt at such a solution was advanced by me some three years ago in my book "Outline of the theory of organic chemistry" (State Chemical Press, 1949). The present article deals with A. M. Butlerov's theory of chemical structure in the light of the recent publication of the volume "A. M. Butlerov. Selected works on organic chemistry" (USSR Acad. Sci. Press,1951) and of the Report of the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences "The state of the theory of chemical structure in organic chemistry" (USSR Acad. Sci. Press, 1951).

I. A.M. Butlerov's Theory of Chemical Structure

A great event has recently occurred in Soviet chemistry--the publication of the volume of A.M. Butlerov's selected works. At last wide circles of Soviet chemists have the opportunity of making direct acquaintance with the theory of chemical structure that served as a guiding star in the development of chemistry nearly 100 years ago. The book is beautifully gotten up, and the papers by A.M. Butlerov have been well selected and edited. The editorial articles by A.D. Petrov and by B.A. Kazansky and G.V. Bykov correctly indicate the tremendous significance of A.M. Butlerov's experimental work in the development of applied and theoretical organic chemistry.

The interpretation of the key idea of A.M. Butlerov's theory of chemical structure given by B.A. Kazansky and G.V. Bykov by way of orientation for the reader in evaluating the significance of that theory and as a reflection of the editors' standpoint produces a painful impression, however. In the conclusion of their article, B.A. Kazansky and G.V. Bykov write: "Naturally enough, the theory of chemical structure has not retained all of its original classical form and has undergone further development. Though A.M. Butlerov found it necessary to distinguish between the concept of chemical structure and the spatial arrangement of the atoms within a molecule...this (such a distinction--G.Ch.) lost any significance for the modern theory of structure long ago. When contemporary theory discusses the structure of a molecule of an organic compound, it conceives of it in the literal sense of the word, that is, it refers to the spatial....arrangement of the atoms comprising it... a definite polarity of its component parts, and the like." (p.583-584) [1] Thus, the concept of chemical structure advanced by A. M. Butlerov,that is, the fundamental difference between A.M. Butlerov's theory and the views of Kekule or Kolbe, according to B.A. Kazansky and G.V. Bykov themselves (p. 563), is wrong in the opinion of contemporary chemists.

The idea of chemical structure as some higher, supramechanical law of chemical

[1]) Here and elsewhere in this article, unspecified page references refer to the one-volume edition of A.M. Butlerov's selected works.

phenomena, to the establishment and confirmation of which A. M. Butlerov devoted his life, turns out to be false. According to B.A. Kazansky and G.V. Bykov, it is the mechanical concept of chemical structure as nothing but the spatial arrangement of atoms within the molecule, i.e., the "constitution" theory of A.M. Butlerov's ideological opponents, Kekule and Kolbe, that conforms to contemporary chemical science.

In their endeavor to justify somehow or other their description of A.M.Butlerov as "a great Russian chemist" (p. 583), B.A. Kazansky and G.V. Bykov write that "The concept of chemical structure is not basic to A.M. Butlerov's theory. The central place in that theory is occupied by his postulate of the chemical properties of a compound as a function of its structure....This postulate proved to be wholly revolutionary in its time" (p. 559)..."However, the concept of A.M. Butlerov's concerning chemical structure was a substantial step forward, since...by differentiating the notion of the distribution of the bonds between chemical atoms from the notion of the distribution of the physical atoms in space (the 'relative arrangement of atoms'), it demarcated the real goal of the development of organic chemistry--the establishment of the chemical structure of organic compounds" (p. 558).

B.A. Kazansky and G.V. Bykov regard Butlerov's idea of chemical structure as a lucky mistake that proved to be fertile from the practical standpoint. Kazansky and Bykov try to show that the idea of the dependence of the properties of substances upon the structure of their molecules would be impossible within the confines of a "truly" mechanical concept of chemical structure, such as the arrangement of the atoms in space. In brief, B.A. Kazansky and G.V. Bykov, considering A.M. Butlerov's concept of chemical structure to be erroneous, do all they can (and even more than they can) under these difficult circumstances to prove the decisive part played by his theory in the evolution of organic chemistry.

Acknowledging the good intentions and the heroic efforts of B.A. Kazansky and G.V. Bykov, we cannot but regret that their article is included in the single-volume edition of A.M. Butlerov's selected works. This article hampers a true understanding of A.M. Butlerov's theory of chemical structure. Nor can we fail to regret the publication of the review by B.M. Rodionov in Progress of Chemistry (1951,No.4), in which the article by B.A.Kazansky and G.V. Bykov is appraised enthusiastically. All this aggravates the harm done to Soviet chemical science by the traditional neglect of the great practical and philosophical significance of A.M. Butlerov's theory.

Contrary to the assertion made by B.A. Kazansky and G.V. Bykov, the idea of a supramechanical--chemical--structure of molecules is the cornerstone of A.M. Butlerov's theory. In A.M. Butlerov's historic report "The chemical structure of substances" (1861), he said: "We do not know the connection that exists within complex molecules between the mutual chemical interactions of the atoms that comprise them and their mechanical arrangement...but nevertheless, even if we leave aside the very notion of physical atoms, we cannot deny that the chemical properties of a complex body are chiefly governed by the chemical relations of the elements that comprise it" (p. 71)... "Up to now I thought it possible to modify the well-known rule to the effect that the nature of a complex molecule is determined by the nature, the number, and the arrangement of its elementary constituents as follows: The chemical nature of a complex molecule is determined by the nature of the elementary constituents, their number, and the chemical structure" (p. 72) [1]. "If we now try to determine the chemical structure of substances and succeed in representing it by our formulas, these formulas will be genuinely rational formulas to a certain extent, even if not entirely so. In the light of this, only one rational

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[1]) A.M.Butlerov used the concept of chemical structure to replace that of arrangement. Therein lies the revolutionary nature of A.M.Butlerov's lecture.

formula will be possible for any one substance, and when we know the general laws of the relationship between the chemical properties of substances and their chemical structure, a formula of this sort will express all these properties." (p. 782).

Thus A.M.Butlerov makes a clear distinction between the concept of the mechanical arrangement of atoms within molecules and the concept of chemical structure and, putting aside for the moment the problem of the relationship between mechanical state and chemical structure, he affirms the decisive importance of the latter in determining the distinct multiformity (a single formula of chemical structure existing for every substance) and chemical properties of substances.

In 1863 A.M.Butlerov thought it necessary to exclude any terminological confusion that might lead to confusion of the concepts of chemical structure and the spatial arrangement of atoms. In his comparison of the terms "constitution" and "chemical structure," A.M.Butlerov expresses his preference for the latter, "as it is more characteristic and is not employed in various connotations, like the word 'constitution,' and hence cannot lead to confusion so readily." In a footnote he adds, "The expression 'the topographical position of atoms' current lately hardly seems to be suitable, since it contains the notion of a determination of the position of atoms in space. I see no need for speaking of this arrangement...when discussing the chemical bond between atoms... As the consideration of the spatial position of atoms is immaterial for chemical purposes...the retention of expressions that presuppose this location will only hamper the desirable unification of differing (though in principle similar) views, which is so extremely important for the advancement of science" (p. 85).

Thus, for the sake of the complete elimination of any confusion of the concepts of atom position and chemical structure, A.M.Butlerov is even ready to accept the temporary exclusion of the former concept from discussions of molecular structure.

In 1885, A.M.Butlerov sets forth his most complete definition of the concept of chemical structure, in his paper on "Chemical structure and the 'substitution theory'":

"1) We are fully entitled to speak of the chemical interrelationship between atoms within a molecule as something real. Putting to one side the problem of the nature of this interrelationship and all spatial notions, we agree to call it by the name of 'compound' or 'bond'.

"2) It is only by some difference in this interrelationship (a difference in the manner of the 'bond') that the phenomenon of isomerism can be explained...

"3) The difference defined above is something constant, residing in the molecule, i.e., it is actually present in it, constituting an inalienable and characteristic part of it. It is this very part, i.e., the definite kind of 'bond' between the atoms, that we call constitution or structure and that we have to deal with when discussing isomers. Moreover, the facts support the view that the difference in the structure of isomers involves a differing distribution of the 'bonds' between the atoms within the molecule. It is the distribution of 'bonds' between the atoms in a molecule that has been given the name of 'chemical structure'" (p. 445-446).

Here, basing himself on his discovery of the agreement between the number of possible isomeric formulas for chemical structure and the number of real isomeric substances, A.M.Butlerov categorically asserts that the idea of chemical structure as determined for each substance by the order of the chemical bond between the atoms within its molecule is not a hypothesis, but rather a true reflection of a most important supramechanical rule (putting aside spatial relations) that applies to chemical phenomena. Here the concept of the chemical bond appears as some singular combining-chemical relationship between the atoms within a molecule that is quali-

tatively different from the general spatial-force (mechanical) relationship of the atoms.

Expanding this latter thought, A.M.Butlerov feels he has to clearly distinguish the concept of chemical structure from the concept of the mutual influences, or the force interrelationships, of the atoms within the molecule. With this in mind, A.M. Butlerov points out the qualitative difference in the mutual influences of atoms that are linked directly and indirectly--that between atoms that are linked together indirectly "the relationship we have called a 'bond' union...is not present...this influence will be one of another kind-- we may call it the mutual influence between atoms that are not directly linked together" (p. 451-452).

It is evident that A.M.Butlerov again and again stresses the supramechanical meaning of the concept of chemical structure. This concept is not equivalent to the concept of the spatial relationships of the atoms nor to the concept of force relationships--" mutual influences." It is clear to A.M.Butlerov that spatial and force--mechanical--relationships are present to a greater or lesser degree among all atoms--within a molecule as well as between molecules, i.e., they are universal relationships. What is more, his discovery of the equivalence of the number of possible chemical structural formulas to the number of real substances convinced A.M.Butlerov that these formulas, as true reflections of molecular structure, furnish direct evidence of the qualitative difference between the relationships of various atoms.

Thus, A.M.Butlerov exhaustively describes the fundamental distinction between his concept of chemical structure and the concepts of space or force interrelationships of the atoms within molecules--the concept of a mechanical molecular state.

All of A.M.Butlerov's creative work is permeated by the idea of the irreducibility of chemical structure to a mechanical state and by the idea of the decisive importance of supramechanical laws in chemical phenomena. To say that this idea is of minor importance in A.M.Butlerov's theory of chemical structure, as is done by B.A.Kazansky and G.V.Bykov, is a crude distortion of Butlerov's theory.

Not only do B.A.Kazansky and G.V.Bykov distort A.M.Butlerov's theory, but they immeasurably minimize the practical and philosophical significance of this theory. At the close of the second citation from the article by B.A.Kazansky and G.V.Bykov cited above, they say that although Butlerov's concept of chemical structure was a false one, it nevertheless was "substantial step forward," since it "demarcated the real goal of the development of organic chemistry--the establishment of the chemical structure of organic compounds."

Everything is in confusion in this evaluation. The real goal of the development of organic chemistry is, of course, not "the establishment of the chemical structure of organic compounds," but mastering the laws of chemical motion in nature and guiding this motion in directions useful to man. Evidently, B.A.Kazansky and G.V.Bykov are not speaking of the goal of the development of organic chemistry, but of the method of its development. Kazansky and Bykov state that A.M.Butlerov's erroneous concept of chemical structure proved to be useful notwithstanding, since it led to the discovery of the most important method in the development of organic chemistry--the method of establishing the structure of organic compounds from their chemical properties (cf. the quotations at the beginning of this article.)

This definition of the most important method in the development of organic chemistry is just as untrue as all the rest. The most important method in the development of organic chemistry is not the establishment of the structure of organic compounds from their chemical properties, but an understanding of the laws of

chemical structure in the multiplicity of organic compounds and thus predicting hitherto unknown substances. It is precisely in their search for the causes governing the possible existence of molecules of various atomic composition, as well as the possible existence of a certain multiplicity of compounds of the same atomic composition, that chemists have discovered the rules of valence numbers, of the octet, the tetrahedron, coordination numbers, coordination, the octahedron, asymmetry, free rotation, and shared and unshared doublets, the combination of which has built up chemists' knowledge of the rules governing the chemical structure of molecules. Formulas for chemical structure subordinated to the foregoing rules proved to be excellent tools to express and predict the individual multifariousness of substances. As for the "method of determining the structure of substances from their properties" or vice versa, this method plays a subordinate role in the development of organic chemistry--the feasibility of using this method depends upon the securing of information on the laws of chemical structure by the first method.

In their paper, B.A.Kazansky and G.V.Bykov depict A.M.Butlerov's theoretical concept as a sort of collection of opinions without any clear logical connection between them. As a result, they have been unable to provide a correct estimate of A.M.Butlerov's theory of chemical structure.

Let us briefly examine the history of the origin and the contents of A.M.Butlerov's theoretical ideas.

We know that structural formulas were written long before A.M.Butlerov. Depicting the valency of atoms by lines and connecting the lines together, chemists explained why atoms do not combine in any quantitative proportions within molecules, but only in certain ones. But the metaphysical thinking of the chemists of the time contained no other notion of molecules than that of mechanical aggregates of atoms coupled in space. Structural formulas, directly expressing some peculiar supramechanical interaction between atoms linked together by valence bonds, were regarded as convenient tools for expressing ways of securing chemical properties or, possibly, the distribution of atoms within molecules, but no one believed that they had any real meaning. The tool that was fated to become the most important tool in chemical science was ready to hand, even though in an extremely crude form. Yet they did not know how to use it.

This knowledge was discovered by A.M.Butlerov. In his study of isomerism, Butlerov discovered that the number of possible structural formulas corresponded to the numerical multiplicity of the real substances. He concluded that structural formulas are not convenient fictive symbols, but true, single-valued expressions of real molecules. Hence, the atoms in real molecules, in exact conformity with the structural formulas, are governed not only by general space-force (mechanical) relationships, but also by some special, supramechanical connecting-chemical relationships. Hence, molecules are not mechanical aggregates of atoms, but chemical compounds subordinated to some supramechanical laws. Hence, the concept of molecular constitution as the arrangement of a molecule's atoms in space must be transformed into the concept of the chemical structure of a molecule as a precisely defined sequence of chemical bonds between the atoms within the molecule. Hence, chemical structure is the most important, fundamental, characteristic feature of a molecule's nature, playing a decisive part in determining its specific diversity and properties. Hence, the chemical structure formulas may be used as a powerful tool for expressing and predicting the specific diversity and properties of substances. These are the theoretical notions of A.M.Butlerov as a whole.

It follows from an examination of this concept that A.M.Butlerov's achievements are not confined to the "fortuitous" discovery of "a method of establishing structure from the chemical properties of substances." Actually, A.M.Butlerov discovered the most important method, described above, of perceiving the laws of chemical

structure from the diversity of substances, comprehended the significance of structural formulas as true reflections of molecules, and showed how to use them as tools for expressing and predicting the specific diversity and properties of substances.

This does not exhaust the contributions of A.M.Butlerov to the development of chemical theory. With his concept of supramechanical chemical structure, A.M.Butlerov was able to overcome the metaphysical mode of thought of the chemists who were his contemporaries and thus to establish the only creative dialectical-materialist view of the nature of chemical phenomena. In retaining the epithet of dialectical materialist for A.M.Butlerov while asserting that by now Butlerov's concept of chemical structure is equivalent to the concept of the arrangement of atoms in space, B.A.Kazansky and G.V.Bykov have themselves endorsed mechanism.

B.A.Kazansky and G.V.Bykov do not adduce, nor can they (since there are none), any convincing arguments to prove that in the light of modern science the concept of chemical structure boils down to the concept of mechanical state. Regarding molecules as some sort of mechanical aggregates of electrons and nuclei, B.A. Kazansky and G.V.Bykov bypass the question of why these "aggregates" are incomparably fewer than the number of arrangements of electrons and nuclei that are efficient from the standpoint of energy. Rejecting the supramechanical laws of molecular structure as governing the real diversity of molecules and unable to explain this multiformity on the basis of mechanical notions, Kazansky and Bykov take an agnostic position. The laws of chemical structure take on the significance of something handed down from above--unknowable.

By way of proving the correctness of the mechanical concept of chemical structure, Kazansky and Bykov simply refer to the alleged point of view of contemporary chemists. Most contemporary chemists, however, regard structural formulas not merely as conventional and inexact expressions of interatomic distances and bond angles within molecules, but rather as, above all, direct and accurate expressions of the order of the chemical bond linking atoms within real molecules, i.e., in the sense of the Butlerov theory of chemical structure. By "contemporary chemists" Kazansky and Bykov apparently mean only the adherents of the mesomerism-resonance theory of Ingold and Pauling, whose concept of chemical structure is the same as the mechanical concept of Kazansky and Bykov.

The article by Kazansky and Bykov is useful in that it provides an opportunity for defining certain important positions in the current discussion on the problems of chemical structure. Until recently, our domestic supporters of the theories of Ingold and Pauling have categorically rejected the contrast between the theory of chemical structure and the mesomerism-resonance theory given by me (in my Outline of the theory of organic chemistry, 1949) based upon the differences in the concepts of chemical structure employed in these theories. In their articles, the "contemporary chemists" constantly alleged that considering structural formulas as nothing but inexact expressions for the spatial relationships between atoms (or electrons and nuclei) within molecules is in full agreement with the meaning A.M.Butlerov gave them.

Against the background of Butlerov's own definitions of the concept of chemical structure set forth in the one-volume edition, Kazansky and Bykov have been compelled to acknowledge that this concept of chemical structure does not agree with that held by "contemporary chemists." This illustrates the correctness of the above-mentioned contradiction set forth by me. At the same time it indicates that inasmuch as the concept of chemical structure held by "contemporary chemists" is incompatible with A.M.Butlerov's concept of chemical structure, their claims to be his intellectual heirs are out of place. Their concept of chemical structure agrees with the views of A.M.Butlerov's opponents, and they are the latter's intellectual heirs.

Seeing that this uncomfortable state of affairs might be discovered, the "contemporary chemists" are trying to find some way out of the situation. Their last achievement in this direction is the above-mentioned report of the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences to the Conference on the Problems of Chemical Structure convened by the Division of Chemical Sciences. The report states: "The concept of chemical structure introduced by Butlerov by no means boils down to a notion concerning the arrangement of atoms and the distribution of bonds within a molecule. Butlerov repeatedly stressed the need for taking the existence of mutual influences between the individual atoms and groups of atoms within the molecule into account" (p. 6 of the Report).

All of this, it is clear, has nothing to do with the Butlerov definition of chemical structure, which Butlerov distinguished sharply from the concepts of the "arrangement" and the "mutual influence" of atoms within molecules, from the concept of the space and force (mechanical) relationships between atoms within molecules. The Commission combines the concept of the distribution of bonds with the concepts of the arrangement and mutual influence of atoms into a single, allegedly Butlerovian, concept of chemical structure in order to reduce the former--supramechanical--concept to the latter--mechanical--one. As a result of this combination, the concept of the distribution of bonds acquires the meaning of the distribution of the most significant space-force interactions between atoms, while the chemical bond becomes nothing but a quantitative species of the universal general mechanical interrelationships between atoms. The concept of chemical structure is reduced to the status of the mechanical concept of the arrangement of atomic nuclei and electronic density within molecules. The sole difference between the concept of chemical structure held by B.A.Kazansky and G.V.Bykov, on the one hand, and that held by the Commission of the Division of Chemical Sciences is that in the latter the concept of chemical structure is not rejected outright, but is reduced to the level of the concept of mechanical state--in a cautious form. This permits the "contemporary chemists" to maintain for the time being their version that their views are in conformity with the Butlerov theory.

II. New Achievements of A. M. Butlerov's Theory of Chemical Structure

As we have indicated above, the Butlerov method of learning the laws of chemical structure from the multiformity of substances was the method of development of the theory of organic chemistry. That is how A.M.Butlerov established the structural theory, and that has been how it evolved subsequently. The discovery of excess substances over the number of possible structural formulas led to the evolution of the structural theory into the stereochemical theory with its tetrahedron and free rotation rules. The discovery of the multiformity of substances that did not fit into the framework of the rules of valence numbers and the tetrahedron led to the evolution of the structural theory into the coordination theory with its rules of coordination numbers and the octahedron. The discovery of ions and radicals, electrolytes and non-electrolytes, resulted in the evolution of the structural theory into the electronic theory, in which the notion of two kinds of chemical bonds was advanced: covalent bonds, formed by the sharing of an electron pair in a two-atom orbit and governed by the valence number, octet, and tetrahedron rules; and electrovalent bonds, formed without the sharing of an electron pair in a diatomic orbit (the duplet remaining within the valency shell of a single atom) and governed by the coordination number, coordination, and octahedron rules. The structural, projection, coordination, and electronic formulas of these theories proved adequate for expressing and predicting all the known multiformity and properties of molecules.

During the evolution of the structural theory into the above-mentioned theories we learned how much the mechanical state of molecules depended upon their chemical

structure. The tetrahedron and octahedron rules, discovered chemically (by means of the Butlerov method described above), explained the way in which the bond angles in molecules depended upon the way in which the atoms were linked together. New physical methods made it possible to measure the bond angles and interatomic distances directly, thus confirming the foregoing rules that had been discovered chemically and adding to them the rules governing the variation of the bond lengths (the interatomic distances) with the nature and multiplicity of the bonds. The discovery of these ways in which mechanical state is a function of chemical structure has made the chemical structure formula suitable for judging the arrangement of the atoms within a molecule.

It is obvious that as a result of all this the chemical structure formula has not remained the same. It has retained the significance of a direct and true reflection of the sequence, order (in the configuration sense), multiplicity, and manner of chemical bonding of the atoms within the molecule. Neither the structural formula nor the projection, nor the coordination, nor the electronic formula expressed anything else directly. Judgments from this formula concerning the methods of synthesis, the mechanical state, and the properties of a molecule are mediated by our information concerning their dependence upon chemical structure.[1])

Unfortunately, the neglect of A.M.Butlerov's theory and ignorance of the history of the development of structural problems has made it possible for "contemporary chemists" to see in the chemical structure formulas nothing but expressions of the mechanical state of molecules. When the "contemporary chemists" learned that there existed a supramechanical concept of chemical structure due to A.M.Butlerov, they regarded it as merely outmoded nonsense. They did not take the trouble to reflect that the formulas of chemical structure were governed by rules determining the localization of electron orbits in one or two atoms, the rules of valence and coordination numbers, the tetrahedron and octahedron rules, the octet and coordination rules, the rules of free and restricted motion of atoms in space--rules that are not explainable from the mechanical standpoint. They did not take into consideration the fact that the reality of the supramechanical rules of molecular structure set forth in these rules has been corroborated by the practical employment of formulas based upon these rules in predicting hundreds of thousands of hitherto unknown molecules. The "contemporary chemists" regarded the chemical structure formulas merely as some unknowable, conceptual standards of energetically efficient arrangements of atomic nuclei and electron densities within atoms.

In this scheme everything was very highly oversimplified. They regarded the molecule as an electronic-nuclear aggregate whose properties were determined by its mechanical state. Once they ignored the rules of chemical structure specified above, the possibility arose of "explaining" the various discrepancies between the chemical structure formulas and the experimental data on the arrangement of the nuclei and the electron density within the molecules or on the properties of molecules by some sort of shifts of the nuclei and electron densities in molecules from conceptual standards. In the Ingold formulas, shifts of this sort are represented by bent arrows, while the Pauling formulas represent them by superposing several standards.

Equipped with these formulas, the mesomerism-resonance theory entered chemistry flying the flag of the mechanistic postulate of the delocalization of electrons and bonds within molecules, setting forth the fictitiousness of the classical formulas of chemical structure with their single-valued, localized electron orbits and chemical bonds.

[1]) Within the confines of the known ways in which mechanical state is a function of chemical structure, there still is an infinity of mechanical states corresponding to each chemical structure formula and differing in the arrangement of the nuclei about the axis of free rotation and in the polar distributions of electron density about the nuclei.

As might have been expected, the mechanical mesomerism-resonance theory proved to be practically sterile. Its viability is due solely to the possibility discovered within the Ingold and Pauling formulas of parasitically employing the stipulatedly fictitious formulas of chemical structure in their usual real meaning. It is apparent that an approach of this sort has no practical advantages. All it does is to make the multiformity and properties of molecules depend upon fictions--the real molecules and the properties turn out to be products of the mind. The mechanism inevitably evolves into the idealism of Machian doctrine.

The methodological defectiveness of the mesomerism-resonance theory is due to the concept of mesomerism that lies at the core of the theory, i.e., the intermediate structure of real molecules when compared to ideal standards. It is upon this concept that the methods of expressing real structures employed in the Ingold and Pauling formulas are based: via "fictitious formulas," which are then used in their real meaning.

A subsidiary role is played by the notion of resonance or disturbance, i.e., some "phenomena," involving an increase in energy, that cause a shift of the nuclei and the electron density from the ideal standards. These concepts make visible the reality of the allegedly fictitious formulas and thus facilitate their parasitical use in their real significance.

The report of the Commission of the Division of Chemical Sciences referred to above is curious because of the way in which the commission, while acknowledging the practical sterility and methodological defectiveness of the mesomerism-resonance theory, contrives to rescue it intact and whole.

The commission criticizes the mesomerism-resonance theory in so far as resonance and perturbation are concerned. The commission correctly points out that inasmuch as the chemical structure formulas used in the Ingold and Pauling formulas are fictitious, the concepts of resonance or perturbation phenomena in the structures corresponding to these formulas are likewise fictitious. The commission proposes that the concepts of resonance and perturbation be discarded from the Ingold and Pauling formulas, and that these formulas be considered simply as expressions of real arrangements of nuclei and electron density as compared with conceptual standards--comparative abstractions (p. 38 of the report).

But how can we then explain the reason for the shift of nuclei and electron densities away from the standards in real molecules? The way out of the impasse was found in the concept of mutual influence. The commission explains this shift as due to the phenomena of mutual influence in the ideal standards, which is accompanied by an increase in energy. But there cannot be any real phenomena in conceptual standards!

The ring has been closed. The commission does not realize it only because it has no doubt about the reality of the concept of mutual influence. It is obvious that this concept, which has been widely used by chemists for a long time to explain singularities in the properties of molecules, is not without real meaning. But concepts are not real by and of themselves, but only in connection with the phenomena that they reflect. The concepts of resonance and of perturbation are likewise real in their proper place. They become fictitious only in the sense of phenomena occurring in conceptual standards. In the same manner, the concept of mutual influence, though a more "chemical" notion, is just as fictitious as the concepts of perturbation and resonance when used to refer to phenomena occurring in conceptual standards.

The commission's desire to save the mesomerism-resonance theory is so strong that it deems it possible to eliminate the practical sterility and methodological

defectiveness of Ingold's and Pauling's theory simply by substituting the words "mutual influence" for "resonance" or "perturbation." We must acknowledge the inventiveness of the "contemporary chemists" in their efforts to evade the necessity of admitting their errors. But one might have expected something more substantial from the report of the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences.

A.M.Butlerov wrote: "...the facts that are not explainable by existing theories are most valuable for science, and the development of the latter in the near future must be expected to result principally from the exploration of these facts" (p.425).

Recent facts of this sort in organic chemistry have been the experimental data secured by physical methods that doubtless indicate a discrepancy between the generally accepted formulas for conjugated compounds (including the aromatics) and the actual mechanical state of their molecules. The exceptionally great importance of these findings is illustrated by the fact that there are hundreds of thousands of conjugated compounds, constituting a large proportion of all organic substances. It cannot be said, of course, that chemists have been wholly satisfied with the generally accepted formulas for conjugated compounds, such as Kekule's formula for benzene, even before the publication of these findings. Such formulas did not allow for the absence of the isomeric ortho disubstitution derivatives of benzene, the saturation of aromatic rings, the orientation phenomena of benzene-ring substitutions, the orientation phenomena of additions to conjugated systems, and for many other "singularities" of conjugated systems, grouped under the general concept "of an aromatic nature."

There was no urgent need for replacing the generally accepted formulas by new ones. Even if we ignore for the moment Kekule's oscillatory hypothesis, the absence of any ortho disubstitution derivatives of benzene might be explained as due to the instability of the second isomer--its pseudomeric relationship to the first one. Even if we ignore the hypothesis of alternating polarity, the orientating properties of conjugated systems might be explained as due to the production of ionized quinone structures that were pseudomers of the usual ones in the reactions. In this manner the major discrepancy could be explained away within formulas with localized orbits and within the concept of tautomerism (pseudomerism).

The situation was not so good insofar as the findings on the stability or saturation of conjugated systems were concerned. To explain these findings they had recourse to Thiele's formula, which crudely violated the valence and octet rules. It is curious that the practical importance of Thiele's formula was confined to this merely episodic role, the usual formulas continuing to be employed in representing molecules and reactions. The lack of faith in Thiele's formulas was so great that even the concept of conjugation did not acquire its sole possible real meaning--a continuous multiplicity of bonding between the atoms of conjugated systems--but retained a purely formal content that explained none of their singularities--an alternation of single and multiple bonds in conjugated systems. In essence, chemists associated the notion of the alternation of single and multiple bonds with various singularities in the properties of substances and simply ignored the problem of the origin of these singularities: of an aromatic nature, and so forth.

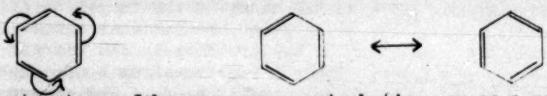
The exceptional importance of the above-mentioned findings, secured by physical methods, lies in the fact that they have made evident the continuous multiple bonding of atoms in conjugated systems. The substitution of new formulas that directly express the continuous multiple bonding of the atoms in conjugated systems for the generally accepted formulas for conjugated compounds, with their alternating single and multiple bonds, has become obvious.

As will be shown below, these new formulas can be found within the framework of the Butlerov theory of chemical structure. Regrettably enough, the Butlerov theory has been forgotten, and it is the mechanistically minded "contemporary chemists" who have busied themselves with the search for new formulas.

The "contemporary chemists" have made use of the data obtained by physical methods to proclaim the fictitiousness of the chemical structure formulas and to affirm the correctness of the Thiele formulas, with their delocalized orbits and bonds. It was soon found, however, that the Thiele formulas were of no use in explaining the orientating properties of conjugated systems. It was the Ingold and Pauling formulas that managed to "eliminate" this contradiction. These formulas made it possible to continue using the previous chemical structure formulas to describe the properties of conjugated systems. The convenience of the Ingold and Pauling formulas lay in the fact that in explaining the "equalization" of the bonds and the "decrease" of energy in conjugated systems, the chemical structure formulas entering into the Ingold and Pauling formulas could be set down as fictions, wholly equivalent to the Thiele formulas.

This apparent way out of the difficulty proved to be a blind alley. At bottom, the episodic attraction of the concept of fictitiousness plays the same role as that formerly played by the episodic attractiveness of the Thiele formula.

The mesomerism-resonance theory does not provide any new formulas for the chemical structure of conjugated compounds but merely a modernized way of circumventing such formulas. All we need do to convince ourselves of the unsatisfactoriness of the Ingold and Pauling formulas as expressions of the structure of conjugated compounds is to examine the mesomeric and resonance formulas for benzene:



Expressing the structure of benzene as a perturbation, or as a resonance, or as a mutual influence in the molecule of the hydrocarbon cyclohexatriene does not resolve the problem of the structure of benzene but merely glosses over it.

As might have been expected, the mechanist approach to the problem of the chemical structure of conjugated compounds proved to be fruitless. The Thiele formulas could not reflect the findings on the orientating properties of conjugated compounds, while the Ingold and Pauling formulas, ignoring "the facts that are most valuable for science," constituted a brake upon the development of organic chemistry, no matter what the trappings with which they were presented.[1]

The new data secured by physical methods, together with the data on the "singularities" of conjugated systems that have been common knowledge up to now, must be reflected in the new formulas for the chemical structure of conjugated systems if these latter are to encompass all the available data. These new, true, formulas must be a straightforward and single-valued expression of the chemical interrelationships among atoms and among atoms, electrons, and nuclei within molecules--the chemical structure of conjugated compounds.

Within this framework, let us consider the central problem--the structure of benzene. The only possible, and practically complete, formula for benzene on the basis of contemporary electronic and nuclear concepts is the benzene formula reproduced herewith. This formula expresses the alternation of positively and negatively charged carbon atoms in the benzene ring, identically linked to each other by double electrovalent-covalent homopolar bonds. This formula makes use of the classical concept of electrovalent bonds, established without the sharing of

[1] Mechanism is thus not merely the gnoseological root of idealism in chemistry, but also hampers its development.

electronic duplets in two-atom orbits, so that it does not violate the rules of the localization of electron orbits in one or two orbits, of the octet, and of valence numbers. This formula combines all the experimental data on the properties and the mechanical state of benzene, of its analogs, its homologs, and its derivatives. And, lastly, this formula, directly and unequivocally expressing the sequence, the multiplicity and the manner of the atomic bonds, fully conforms with the Butlerov concept of chemical structure.

There are three obstacles to the recognition and spread of the formula cited. The first is of a superficial nature. Inasmuch as the concept of an electrovalent bond is usually associated with the notion of bond polarity, the formula will be regarded as failing to agree with the presence of an axis of symmetry of the sixth order in the benzene molecule. If we bear in mind that the plus and minus signs in the cited formula represent the atomic charges rather than the electron distribution, the first--superficial--obstacle to its adoption is eliminated automatically.

The second impediment is more serious. We have to overcome the customary notion of the electrovalent bond as that of a polar bond. We have to convince chemists of the feasibility of a homopolar electrovalent bond.

Notwithstanding the apparent paradoxicality of the concept of a homopolar electrovalent bond, it has a logical foundation. Let us start with the classical notion of an electrovalent bond as one formed by the sharing of an electron pair in a two-atom orbit. Within this framework we cannot reject the assertion that in the formation of an electrovalent bond between two equally electronophilic atoms (say, between two carbon atoms), the electron density ought to be distributed uniformly owing to the deformation of the electron shells of the atoms. There remains the problem of what may serve as the cause of the formation of an electrovalent bond between equally electronophilic atoms, rather than a covalent bond. The answer may be found in a comparison of the new formula for benzene with the hexatriene formula for its pseudomer. The six electrovalent bonds doubtless represent an increase in energy over three covalent bonds. The reason for the formation of an electrovalent bond between equally electronophilic atoms may be the increase in energy that accompanies the conversion of one covalent bond into two electrovalent bonds. Thus, the concept of a homopolar electrovalent bond is not logical nonsense. The reality of this concept is given by the fact that it is the only one that opens up the possibility of providing a practically and methodologically complete solution of the problem of the structure of conjugated compounds.

The third obstacle to the adoption of the formula we have cited is of an ideological nature. The justification for the concept of a homopolar electrovalent bond is founded upon the notion of the supramechanical phenomenon involved in the attachment of electrons to nuclei. This concept is in conformity with the Butlerov concept of chemical structure--the qualitative difference between the relationships of linked and unlinked atoms being due to the qualitative difference in the relationships between the electrons and the nuclei. From the mechanical standpoint, however, the attachment of electrons to nuclei is a matter of the distribution of electron density about the nuclei, so that the notion that, in addition to the general space-force relationships between electrons and nuclei within molecules, there exist some other, peculiarly combining-chemical relationships does not enter the mind of the "contemporary chemists."

Decisive proof of the reality of the notion of supramechanical relationships between electrons and nuclei is afforded by the fact that the dependable formulas of chemical structure, with orbits localized in one or two atoms, which have been tested in a vast number of experiments, become fictions outside the framework of this notion.

Inasmuch as only the Butlerov affirmation of the truth of chemical structure formulas leads to an understanding of the laws of chemical phenomena and to a mastery of these rules for practical ends, as the history of the development of organic chemistry has shown, it is evident that the notion of supramechanical relationships between electrons and nuclei conforms to reality.

These are the three obstacles to the adoption and the spread of the benzene formula cited above. They will be overcome. This formula deserves to live, since it alone provides a way out of the practical and methodological blind alley into which chemical theory has been led by the "contemporary chemists." The solution of the problem of the structure of conjugated compounds provided by this formula is another splendid triumph of A. M. Butlerov's theory of chemical structure.

A. M. Butlerov wrote: "Now that we have established the major facts, it will not be wholly superfluous to say a few words about a minor matter--formula notation. Remembering that what matters is not the form, but the essence, the concept, the idea, and bearing in mind that the formulas representing isomerism must logically express actual molecules, i.e., certain chemical relationships existing within them, we readily see that any notation may be satisfactory, provided it satisfactorily expresses these relationships... If terms are not defined adequately, however, another notation may result in misunderstandings" (p.455).

The notation comprised in the Ingold and Pauling formulas has resulted in a quandary pregnant with evil consequences. The wide acceptance of the mesomerism-resonance theory has been due to the fact that most chemists have erroneously taken the curved arrows in Ingold's formulas to be merely graphic symbols of the order in which the electron orbits are redistributed during reactions, while the double-ended arrows of Pauling's formulas have been taken to be merely graphic symbols of the tautomeric and equilibrium interrelationships of structures connected by these arrows. To avoid perplexities, we now have to stop using the Ingold and Pauling formulas. The employment of curved and double-ended arrows as graphic symbols without any mesomerism-resonance significance should be postponed until the Butlerovian significance of chemical structure formulas has been clearly understood.

Strange though it may seem, the significance of chemical structure formulas still remains unclear. The possibility of judging the methods of synthesizing substances and their properties as well as the mechanical states of molecules, from chemical structure formulas has created the impression that these formulas are the direct expressions of these methods, properties, and states. The plurality or the variability of the latter has led to the conclusion that the chemical structure formulas are inexact and have to be developed into Ingold or Pauling formulas. The single-valued numerical correspondence between the formulas of chemical structure and the molecules is lost, and chemical theory is transformed into a Machian scholasticism.

We must understand the decisive significance of Butlerov's principle of the direct and single-valued representation of molecules for the scientific classification of known substances and the prediction of unknown ones--for chemical theory. Butlerov's idea of chemical structure has the qualities of genius because he was able to find, among the multiform and variable characteristics of molecules, the one major and only invariant characteristic that defines the discreteness and specificity of the molecule, the loss of which suddenly transforms the molecule into a different one. Butlerov discovered the meaning of a chemical structure formula as a scientific abstraction that truly and

directly expresses the qualitative definiteness of a molecule and thus converted this formula into one of the most important tools for the development of chemistry.

It must be borne in mind that that a chemical structure formula is not abstract in the sense that such a formula alone is not enough to represent clearly the given states and properties of a molecule (that is the meaning in which the term "abstraction" is employed in the report of the Commission of the Division of Chemical Sciences), but rather in the sense that it directly expresses nothing but the chemical interactions of atoms with atoms, electrons with nuclei, within molecules; a chemist's judgments, of given methods, properties, and states (or conversely) from this formula are mediated by his knowledge of how the latter depend upon chemical structure and are governed by the decisive importance of the qualitative definiteness of the molecule for all its other multiform and variable characteristics. Efforts to transform a chemical structure formula into an expression of multiform and variable mechanical states or chemical properties are absurd and harmful.

Full comprehension of Butlerov's idea of chemical structure is needed to avoid the serious quandaries which result from the Ingold and Pauling formulas.

In conclusion, it may be useful to define the interrelationships of the various theories aiming to solve the structural problem. The structural, stereochemical, coordination, and electronic theories, enriched with the Butlerov concept of chemical structure, constitute in the totality A. M. Butlerov's theory of chemical structure; therein lie the developments of the future. The "new structural theory" I have advanced is nothing but a refinement of the electronic theory in the light of the Butlerov theory of chemical structure and an endeavor to apply this theory to solve the problem of the structure of conjugated substances.

As for the mesomerism-resonance theory, in all its modifications, it is the direct opposite of A. M. Butlerov's theory of chemical structure and represents nothing but an expression of a mechanistic viewpoint in chemistry, an unscientific Machian concept that is sterile in practice.

A. M. Butlerov's theory of chemical structure resembles D. I. Mendeleev's periodic system in that the latter reveals the supramechanical laws governing atomic structure, thus making it possible to predict the multiformity and properties of atoms, while the former reveals the supramechanical laws governing molecular structure, thus making it possible to predict the multiformity and properties of molecules. The theories of D. I. Mendeleev and A. M. Butlerov, in combination, provide a practically and methodologically complete solution of the most important problem of chemical theory--the structural problem.

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